SMITH'S
COLLEGE CHEMISTRY
REVISED AND REWRITTEN

BY

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PREFACE TO THE FIRST EDITION

THE present work differs from the Author's "Introduction to
General Inorganic Chemistry" in being intended for pupils who
can devote less time to the study of the science, and whose needs
can be satisfied by a less extensive course. 'It resembles the
larger work in the arrangement of the contents and in the general
method of treatment. The matter, and particularly the theoreti-
cal matter, however, has been simplified and has been confined
strictly to the most fundamental topics. Such parts of the theory
as are thus given are presented with the same fullness as before
and are illustrated and applied with all the persistence needed to
insure full apprehension and, ultimately, spontaneous employ-
ment by the student. Such parts as could not be treated in this
way, within the limits set by the plan of the book, have been
omitted. Methods materially different from those used in the
"Introduction" have been employed in presenting many topics.
Conspicuous differences of this kind will be noted particularly in
the treatment of combining proportions, formulæ and equations,
molecular and atomic weights, chemical equilibrium, ionic sub-
stances and their interactions, and the theory of precipitation.

The writer desires to express his profound gratitude to the
many chemists who have made valuable criticisms and sugges-
tions. Most of these comments applied to the "Introduction to
General Inorganic Chemistry," but many of them have been used
in preparing this work (General Chemistry for Colleges), and all
will be considered in the second edition of the larger book.

For critical reading of the whole of the proofs of the present
work, the writer desires especially to thank Messrs. A. T. McLeod
and Alan W. C. Menzies of the University of Chicago. Other
corrections and suggestions will be gladly received by the author.

ALEXANDER SMITH.

Chicago, April, 1908.

PREFACE TO THE REVISED EDITION

In preparing this edition for the pr. , practically the entire book has been re-written, but at the same time every effort has been made to leave the volume a characteristic Smith text. In the early chapters, particular attention has been paid to a re-statement of the fundamental conceptions of molecular and atomic weights. The development of these topics in earlier editions has been pretty generally criticized, and it is hoped that the method of presentation here substituted will be found more simple by the student and more logical by the teacher. The chapters on solution and ionization have been re-arranged and expanded in accordance with the modern view-point. In the latter half of the volume, the chemistry of the more familiar carbon compounds has been treated in somewhat greater detail than is customary in text-books of General Chemistry, in order that students who are going no further into the subject may not miss the opportunity of correlating their knowledge with the facts of everyday life. The review of recent advances in the final chapter is not intended to be exhaustive, and if it succeeds in impressing only a small percentage of its readers with the desire to discover what chemistry has to offer beyond the limits of the present course it will have amply fulfilled its purpose.

Many sections have been introduced dealing with newly-developed and important industrial processes, and with the application of chemistry to modern warfare. The diagrams throughout the text have been improved and increased in number. To assist the beginner in making a thorough examination of his grasp of the subject *during the course*, two chapters (XXXII and L) have been inserted, in which practical methods of identifying substances by means of their distinctive properties and reactions are briefly presented. These review chapters are

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not meant to supplant the actual carrying out of the experiments described in the laboratory, but should serve to co-ordinate more clearly in the mind of the student the theoretical and the practical aspects of the science. This co-ordination may be extended over the whole course by employing the revised edition of Smith's *Laboratory Outline of College Chemistry* in conjunction with the present text.

Thanks are extended to Dr. E. D. Crittenden for assistance in correcting the proof.

JAMES KENDALL.

New York, February, 1923.

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ILLUSTRATIONS

When Alexander Smith was awarded the honorary degree of
LL.D. by his *alma mater*, the University of Edinburgh in 1919,
he was introduced at the graduation ceremonies as follows: "A
most distinguished graduate of our own University, Professor
Smith has risen to the rank of a super-chemist in the United
States, head of a department embracing many specialized pro-
fessorships, and director of one of the most important labora-
tories in the new world. We congratulate Columbia University
on the possession of a teacher and instructor of such rare ability,
and we congratulate ourselves on the opportunity of laureating
an alumnus whose success reflects no little luster on the institu-
tion where he received his early training."

As a member of the aristocracy and a former government official,
Lavoisier, "the father of modern chemistry," was brought to trial
in Paris during the Reign of Terror and sentenced to die on the
guillotine within twenty-four hours. When the presiding judge
was petitioned to delay the execution in order that Lavoisier
might complete some of his work, the retort was made: "The
Republic has no need of chemists; let justice take its course!"
Yet only a few years later the French Republic, ringed around
with enemies, was almost at the point of collapse owing to the
lack of chemicals necessary for carrying on the conflict. Common
substances like soda and saltpeter were produced in sufficient
quantity with the greatest difficulty, and a Lavoisier would
have been of even greater service to his country at that time
than a Napoleon.

Arrhenius put forward his theory of ionization while still a
student at Upsala. His own description of its reception is worth
repeating: "I came to my professor, Cleve, whom I admire very
much, and I said: 'I have a new theory of electrical conductivity
as a cause of chemical reactions.' He said: 'That is very interest-
ing,' and then said 'Good-bye.' He explained to me later, when
he had to pronounce the reason for my receiving the Nobel
Prize for that work, that he knew very well that there are so
many different theories formed, and that they are almost all cer-
tain to be wrong, for after a short time they disappear; and
therefore, by using the statistical manner of forming his ideas,
he concluded that my theory also would not exist very long."
It scarcely needs to be added here that the theory is still very
much alive!

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When Dr. Langmuir presented his first paper on the arrangement of electrons in atoms and molecules at the Buffalo meeting of the American Chemical Society in 1919, the opinion was expressed by one of the leading chemists in the audience that the occasion was the most momentous in the history of chemistry since Dalton propounded the atomic theory. Many additional converts were made when he addressed the British Association at Edinburgh in 1921.

Irving Langmuir occupies the post of research chemist in the laboratories of the General Electric Company at Schenectady, N. Y.

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CHAPTER I

THE CHEMICAL VIEW OF MATTER

CHEMISTRY is a science which deals with all forms of matter. It considers the natural kinds, such as rocks and minerals, as well as materials like fat and flour obtained from animals or plants. It deals also with artificial products like paints or explosives. When we wish information about any specimen or kind of matter, we consult a chemist. Now chemists have worked out a point of view which enables them to attack any problem connected with matter in a systematic manner and to state the results in a clear and simple way. To learn something of chemistry, we must acquire this **point of view** and master the **technical language** the chemist uses in stating and discussing his results.

Properties. — Suppose that a piece of **rusty iron** is submitted to the chemist. He at once examines the rust and notes that it is solid, reddish-brown in color and earthy in appearance. He separates some of it from the iron and finds it to be brittle, that is, easily broken and capable of being pulverized in a mortar. He finds that its density is about 4.5, that is to say, 1 cubic centimeter of it weighs about 4.5 grams. On heating some of it in a flame, he finds that it does not melt, and must therefore have a very high point of fusion. These qualities he calls *properties*, and more especially physical properties. Since all specimens of iron-rust show exactly the same properties, he often calls them **specific physical properties**, because they are **properties shown by all specimens of a particular species of matter.**

After removing any rust by filing or scraping, the chemist ex-

amines the iron, and finds a fresh, clean surface to be almost white and metallic in appearance. The metal is tenacious, so that it can be bent but not easily broken. It is ductile and can therefore be drawn out into wire. He finds that its density is about 7.8, and that the metal is incapable of being melted in an ordinary flame. In addition, he finds it to be strongly attracted by a magnet, while rust is not attracted.

The chemist, then, studies what he calls the specific physical properties of each material, in order that he may be able to recognize various materials.

Substances. — All specimens of pure iron show one set of properties, peculiar to iron, and all specimens of iron-rust show a different set, peculiar to rust. The chemist calls **any definite variety of matter, all specimens of which show the same properties, a substance.** Iron is one substance and rust another. A substance is recognized by the specific properties which it exhibits when exposed to various tests.

The point of view of the chemist thus consists in describing any material by ascertaining whether it exhibits the properties of one, or of more than one substance. **He describes it by naming the substances which,** by a study of their properties, he has found in it.

Two Illustrations of the Study and Description of Materials. — If a piece of **granite** is examined by a chemist, he observes
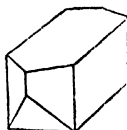
FIG. 1.   FIG. 2.   FIG. 3.

at once that it is spotted in appearance, and made up of several crystalline materials of differing nature. He therefore breaks it up and studies the *properties* of the fragments. Some of the fragments of granite are dark and with a penknife can easily be split into transparent sheets, thinner than paper. These particular fragments are in all respects like *mica* (Fig. 1)   This

substance is a mineral which, in certain neighborhoods, occurs in large masses, and sheets of it ("isinglass") are used to fill the openings in stoves. Others of the fragments are clear like glass, and are very hard, and have *all* the properties of quartz or rock crystal (Fig. 2), which is another substance well known to the chemist. The remaining fragments are less clear than is quartz, and are not so hard. They can be split into layers, but not nearly so easily as can mica. They form oblong crystals, differing in this also from quartz, which shows hexagonal crystals. This substance is *felspar* (Fig. 3). Thus the chemist studies the physical properties of the fragments, and finds that there are three different substances in granite. He reports that the components of granite are mica, quartz, and felspar.

When flour is examined by the chemist, it appears to the eye to be all alike. Under the microscope, even all he can learn is that it consists largely of grains, which have the characteristic appearance of grains of starch (see Fig. 115, p. 515). He places some flour on a square piece of cheese-cloth and encloses it by tying with a thread (Fig. 4). On kneading the little bag in a vessel of water, the water becomes milky. When the milky water stands, the white material settles to the bottom, the water can be poured off, and the deposit can be dried. This white substance, when boiled

FIG. 4.

with water, gives an almost clear liquid which jellies on cooling. This is another property of starch. A little tincture of iodine (solution of iodine in alcohol), dropped on a part of the starch, causes the latter to turn blue. This is a very characteristic property of (and therefore *test* for) starch. When the bag of flour is kneaded persistently in water which is frequently changed, the material finally ceases to render the water milky. The starch has all been washed out. When the bag is now opened, a sticky material is found in it. This is called *gluten.* The chemist therefore finds that the flour contains starch and gluten. He learns this by **separating** the components.

* Crystals (see pp. 105-108) are natural forms, of geometrical outline, which solid substances assume.

Law of Component Substances. — Every material consists of one substance, or is a mixture of two or more component substances, each of which exhibits ∴ definite set of specific physical properties. In terms of these properties the material can be described. This is the first and most fundamental law of chemistry. This conception was first clearly stated by Lomonossov (1742), a Russian author, statesman, and chemist (1711-1765).

Mixtures and Impurities. — A material containing more than one component substance is called a **mixture.** The characteristic of a mixture is that each of the component substances, although mixed with the others, **possesses exactly the same properties as if it were present alone.** No one of the components affects any other component, or alters any of its properties. Granite and flour are typical mixtures.

• The ingredients of a mixture are called the **components** (Latin, *put with*),• because they are simply placed together, without change, and can be separated without change.

When a specimen is composed mainly of one substance, and contains only minute amounts of one or more other substances, it is frequently spoken of as a specimen of the main substance containing certain specified substances as **impurities.** To be called an impurity, the foreign matter need not be dirty or offensive. Thus, common salt usually contains a little magnesium chloride, a white crystalline solid, as an impurity, and it is this impurity which becomes damp in wet weather. Again, compounds of lime and magnesium are common impurities in drinking water.

Specific Physical Properties. — It will be seen that, to the chemist, knowing the physical properties of all substances is very important. By means of the properties, he recognizes and describes all the bodies he studies. It may be well, therefore, here to give a list of the more important properties, most of which have been mentioned in connection with the illustrations we have used.

In the case of **solids**, the chief physical properties the chemist uses are **color, crystalline form, solubility** or **non-solubility in**

water and occasionally other liquids, the temperature at which the substance melts (**melting-point**), and the density.

In the case of **liquids**, he notes the temperature at which the liquid boils (**boiling-point**), the **density**, the **mobility**, the **odor**, and the **color**.

Finally, in the case of **gases**, the properties commonly mentioned are the **color**, **taste**, and **odor**, the **density**, **solubility** in water, and the ease or difficulty with which the gas can be **liquefied**.

Attributes and Conditions. — There are other qualities which a body may possess that we are liable to confuse with the specific properties. Thus, the weight of a piece of sulphur is not a property of sulphur. A hundred pieces of as many different substances might all have the same weight, so that a particular weight (say 2 grams) is not a property of any one species of matter. **Weight, dimensions, and volume are attributes of a particular specimen only.** They have different values for different specimens, even when these are all composed of the same substance. The attributes are physical in nature. They are of great importance in chemistry, however, because **they afford the only means we have of measuring quantities of substances.**

There are still other qualities which a body (or specimen of matter) may possess. It has, for example, a certain **temperature**, **pressure** (state of compression), **motion**, or **electric charge**, and it may be **in solution** in some liquid. A body may change in temperature, pressure, or state of electrification, or it may be dissolved in water, or be recovered by evaporation of the liquid, and yet be the same specimen. A hundred specimens of as many different substances may all have the same temperature — this is not a specific property. These qualities we have just mentioned are all spoken of as **conditions.** The temperature or the pressure of a specimen may be changed at will. But the specific properties of a substance under any given conditions cannot be changed, so long as we have to do with the same substance.

The Rusting of Metals. — If we return once more to the subject of rusty iron, we find another point which interests the

chemist. If the iron is kept moist — for example, by lying in the grass or partly immersed in water — the layer of rust gradually becomes thicker, and the core of iron becomes thinner, until it finally disappears. The rust seems to be *formed from the iron*, in presence of air and moisture. The iron, particle by particle, loses the properties of iron and simultaneously acquires those of rust. Now the chemist is concerned, not only with recognizing substances, but also with the ways in which substances change and new substances are produced.

Several other familiar metals rust, as does iron, but the change is slower. Thus, lead rusts (tarnishes) slowly, and zinc still more slowly. The change can be hastened by heating. For example, if some lead is melted in a porcelain crucible (Fig. 5), a yellow powder collects on the surface. Gradually more and more of the powder is formed and less and less of the metallic lead remains, until at last all the metal is gone. Melted tin, when treated in the same way, gives a white powder.
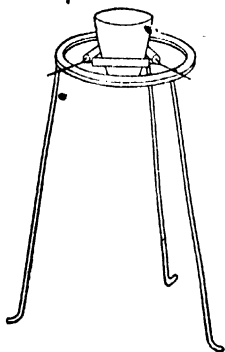
Explanation of Rusting. — The first fact which seemed to throw light on the subject was discovered by a French physi-

cian, Jean Rey (1630), who found that the rusts of tin and lead, made by heating and stirring, were *heavier* than the original pieces of metal. He inferred, correctly, that the additional material which caused the increase in weight came from the air. He imagined, however, that the rust was not a new substance, but a sort of froth, and therefore a mixture of air with the metal. Other investigators, such as Hooke (1635–1703) and particularly Mayow (1643–1679), in England, explained the increase in weight by supposing that some material from the air had *combined with* the metal. In other words, iron, for example, was one substance composed of iron only, and rust was another substance, made by union of iron and a material from the air, and not a mere mixture.

It was Lomonossov (1756) who first proved by an experiment

that the extra material did come from the air. He placed some tin in a flask, sealed up the mouth of the vessel, and weighed the whole. The flask was then heated and the tin was converted into the white powder. So long as the flask remained sealed, no change in weight was found to have occurred. When the mouth of the flask was opened, however, some air rushed in, and the total weight was then found to be greater. Evidently, during the heating, a portion of the original air had forsaken the gaseous condition and joined itself to the tin to form the powder. This left a partial vacuum in the flask, and more air entered when the latter was opened. Eighteen years later the same experiment was made by Lavoisier, who drew the same conclusion. The rusting of other metals was found to be due to the same cause. Lavoisier named the gas, taken from the air, **oxygen.**

The conclusion can be confirmed in various ways. For example, when the air is pumped out of the flask before it is sealed, the metal can be heated in the vacuum indefinitely without rusting.

Experiment to Show the Nature of Rusting. — That a part of the air is consumed when iron rusts is easily proved. We moisten the interior of a test-tube and sprinkle some powdered iron so that it covers and adheres to the whole interior surface. We then set the tube mouth downwards in a dish of water. At first, the pressure of the water compresses the air in the tube very slightly, and the water ascends above the mouth to the extent of a small fraction of an inch only. As the moist iron slowly rusts, however, the oxygen is gradually removed, and the pressure of the atmos-

Fig. 6.

phere outside slowly pushes the water farther up the tube. After an hour or more, the water has ascended about one-fifth of the total distance towards the top of the tube (Fig. 6). However long
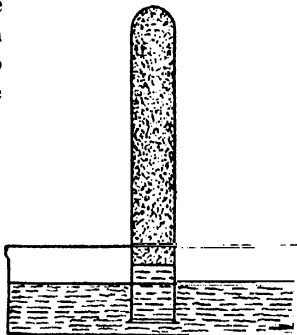
we watch the experiment, and however great an excess of iron we use, the water ascends no farther, while if we make a care-. ful examination of the residual gas in the tube, we find that it exhibits none of the properties of oxygen. Evidently that portion of the air which consists of oxygen has forsaken the gaseous condition, and the water has been forced up to take its place. Inspection of the powder in the tube now shows some reddish particles, where rusting has occurred. The rust, then, is made up of a part of the iron and all of the oxygen that the tube contained. .

Of course, much of the iron powder is unchanged in color, and has not rusted. The air in the tube did not contain oxygen enough to combine with all the iron. The iron that remains is as little able to rust in the remaining gas as in a vacuum.

Incidentally we learn from this experiment that atmospheric air is a mixture, containing about one-fifth (20 per cent) oxygen by volume. The remaining four-fifths is almost all nitrogen (79 per cent), a substance which combines with very few materials, while the balance (1 per cent) is made up of argon and other gases which do not enter into combination with any known substance. If lead, tin, or zinc had been heated in an enclosed volume of air, they likewise would have taken out the 20 per cent of oxygen and would have left the other gases.

The Law of Chemical Change. — The three examples of rusting show that specimens of matter can lose their original properties and acquire new ones. Since a substance is "a species of matter, with a constant set of properties," we are compelled to decide that, when a material *changes* its properties, it has, in doing so, become a *new* substance. This consideration calls to our attention the **second** of the fundamental **laws of chemistry,** namely, that **the material forming one or more substances** (such as oxygen and iron), without ceasing to exist, **may be changed into one or more entirely different substances.** Such a change is called a **chemical change,** or **reaction.**

In chemistry, **conditions** are often altered in order to bring about, or to stop chemical change, or to modify the speed with which it takes place. Thus, we heated the lead (raised its *tem-*

perature) in order to hasten the process of rusting. If a substance, or mixture, is capable of undergoing ordinary chemical change, then the change is always hastened by raising the temperature, and is always delayed or prevented by lowering the temperature. Similarly, changing the pressure in a gas, or dissolving a substance in some liquid, frequently hastens or delays a chemical change in which the substance takes part. The proper physical conditions are, therefore, considered in connection with every chemical operation. **Conditions are used to modify chemical change.**

The commoner kinds of chemical reactions may be divided, for convenience, into four varieties. We can now define the first of these.

First Variety of Chemical Change: Combination. — In each case of rusting, two substances (a gas and a metal) came together to form a third substance (an earthy powder). Apparently two substances may come together in two different ways. They may form a mixture, in which both substances are present and retain their properties, or they may react to form a single substance with different properties. When **two (or more) substances unite to form one substance,** the change is called chemical **combination or union.** The product is called a **compound substance.**

We are very careful never to speak of a compound substance as a mixture. Rust is not a mixture of iron and oxygen; it shows none of the properties of either. Nor do we call a mixture (like granite) a compound, or the operation of mixing, combination or union. These are technical words in chemistry and, to avoid confusion, may be used only with due regard to their technical meanings.

Constituents. — As we have seen, we speak of the substances in a mixture as the components. When we wish to refer to the forms of matter which are chemically united in a compound, we call them the **constituents** (Latin, *standing together*) of the compound substance. Thus, iron and oxygen are the constituents of rust.

The chemist **separates** (p. 5) the components of a mixture, for

.that is all that is necessary. He **liberates** the constituents of a compound, however, because *they* are bound together in chemical combination.

The names given to compounds are usually devised so as to indicate the nature of the constituents. Thus, iron-rust is oxide of iron (or ferric oxide, from Latin *ferrum*, iron). The yellowish powder from lead is lead oxide or oxide of lead, and the white powder from tin is oxide of tin.

A Condensed Form of Statement. — We may represent a chemical combination, or indeed any kind of chemical change, in a condensed form, thus:

Iron + Oxygen → Oxide of iron (ferric oxide).
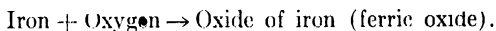
Each name stands for a substance. Two substances in contact with one another (mixed), but not united chemically, are connected by the + sign. The arrow shows where the chemical change comes in, and the direction of the change. We read the statement thus: Iron and oxygen brought together under suitable conditions undergo chemical change into oxide of iron, called also ferric oxide. Similarly we may write:

Lead + Oxygen → Oxide of lead.
Tin + Oxygen → Oxide of tin.
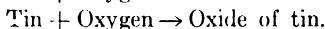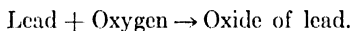
The Increase in Weight in Rusting. — As we have seen, the process of rusting is accompanied by a slow increase in the weight of the solid, due to the gradual addition of oxygen to the metal. Now this increase in weight ceases of its own accord, when a certain maximum has been reached. This occurs when the last particles of the metal have disappeared. Thus, the lead gains in weight until every 100 parts of the metal have gained 7.72 parts of oxygen, and the tin until every 100 parts have gained 26.9 parts of oxygen. When these increases have occurred, the metal is found to have been all used up, and prolonged heating and stirring cause no further union with oxygen and no further change in weight. This fact, that each substance limits itself of its own accord to combining with a fixed proportion of

the other substance, in forming a given compound, is one of the most striking facts about chemical combination. In mixtures, any proportions chosen by the experimenter may be used. In chemical union, the experimenter has no choice; the proportions are determined by the substances themselves. Thus, 100 parts of iron when turning into ordinary red rust take up 43 parts of oxygen, no more and no less.

This fact enables us to make our condensed statements more specific and complete by including in them the proportions by weight used in the chemical change:

Iron (100) + Oxygen (43) → Ferric oxide (143).
Lead (100) + Oxygen (7.72) → Oxide of lead (107.72).
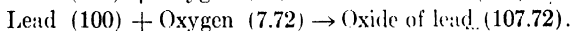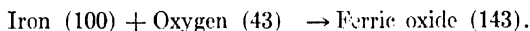
The following numbers, which represent the *same proportions* by weight, are the ones commonly used by chemists, for reasons which will be given later (Chapter IX):

Iron (223.36) + Oxygen (96) → Ferric oxide (319.36).
Lead (414.4) + Oxygen (32) → Oxide of lead (446.4).
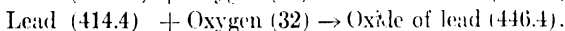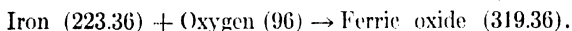
A Word of Warning. — A student who has already obtained in a previous course a clear understanding of molecular and atomic weights, and of their utilization in the writing of formulæ and equations, should be encouraged to exercise his skill by re-writing the condensed statements given above, and those which he will encounter in succeeding sections, in their final chemical form. The figures (other than percentages) added in brackets to these condensed statements are furnished, in point of fact, for the express purpose of assisting such a student. In general, however, it is highly inadvisable to rush a beginner too rapidly through the introductory stages of the science. The statement that the learner wants to employ the tools of his trade as early as possible sounds plausible, but any one who handles tools without a proper appreciation of their use is liable either to cut himself or to injure the tools. The beginner who writes equations without understanding their full significance is almost certain, indeed, to write them incorrectly, and will tend by force of habit to continue to write them incorrectly even after he has been

.taught the principles upon which they should be based. Further-more, the very fact that he has been using formulæ prior to a study of molecular and atomic weights is apt to minimize, in his view, the importance of these fundamental conceptions. Why (he feels) should he be forced to follow every step of the rather involved reasoning by which molecular formulæ are derived and justified, when he has been employing these same formulæ all along without having to bother about theory? If chemistry is to be taught as a logical science, not as a multitude of discon-nected facts, the theoretical development of molecular and atomic weights *must precede* the practical application of these principles in deducing formulæ and making complete equations.

Summary. — Thus far, we have learned that chemistry deals with substances and their physical properties, and with the changes which substances undergo. We have discussed and de-fined a number of important words expressing fundamental chemical ideas. Finally, we have touched upon the weights of the materials used in chemical change, a subject of great importance which will be more fully developed in a subsequent chapter.

Exercises. — 1. Take one by one the words or phrases printed in black type and the titles of the sections in this chapter, and endeavor to recollect what you have read about each. In each case try, (a) to recall the meaning and to state it in your own words; (b) to recall the facts associated with, and the reasoning which lead up to the point in question; (c) to recall examples illustrating the conception and to apply the conception in detail to each example. Whenever memory fails to give a perfectly clear report of the matter in hand, the text must be read and re-read until the essential point can be repeated from memory. Use the same method in all future chapters. A useful prac-tice is to employ a pencil as you read and to underline systemati-cally all the important facts and statements, and then to go back and apply to each marked place the process described above.

2. Define the following terms: Specific gravity, tenacity, melt-ing-point, specific physical property, pure body, vacuum.

·3. Is it logical to say "pure substance"?

4. Why do we decide that granite is a mixture and iron a single substance?

5. Do the statements in the text indicate that air is a mixture or a compound?

6. What weight of oxygen would be required to. convert 25 grams of lead into oxide of lead?

7. Make a list of the technical words we have defined, and place the definition opposite to each.

8. What weight of tin would be contained in ·15 grams of oxide of tin?

9. If any of the following are mixtures, mention the facts which show them to contain more than one substance: (a) muddy water, (b) an egg, (c) milk.

10. In recognizing a specimen to be quartz, does the chemist consider (a) the weight, (b) the temperature, (c) the length of the specimen? If not, why not?

11. Give a list of the specific properties mentioned in this chapter.

CHAPTER II

WE must now take up two new examples of chemical change. They will aid us in introducing one or two additional conceptions and laws. These are continually used by the chemist, and without them, we cannot begin the systematic study of the science.

Another Case of Combination: Iron and Sulphur. — Since oxygen is an invisible gas, there is a slight difficulty in realizing that rusting consists in the union of *two* substances — this gas and a metal. The present example is less interesting historically, but it is simpler because both substances are visible and are easily handled. The case of iron and sulphur will enable us to illustrate the same point of view and to practise the application of the same technical words. It will also introduce us to two manipulations — filtration and evaporation — which are frequently used by the chemist.

We begin by observing the physical properties of the two substances. Those of **iron** have already been noted (p. 4).* **Sulphur** is a pale-yellow substance of low specific gravity (sp. gr. 2). It is easily melted (m.-p. 114.5° C.). It does not dissolve in water — that is, it does not mix completely with and disappear in water, as sugar does on stirring. It does dissolve readily in certain other liquids, such as carbon disulphide, however. It crystallizes in rhombic forms (Fig. 7). It is not attracted by a magnet.

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* References to previous pages are used in order to save needless repetition in writing. The beginner requires endless repetition in his reading, however, and must *form the habit* of examining in conjunction with the current text, the parts referred to. The passages cited are, by the reference, *made part of the current text,* which will usually not be clear without them. The same remark applies to topics referred to by name. Such topics must be sought in the index.

All terms, and especially those borrowed from physics, if not perfectly familiar, must be looked up in a work on physics or in a dictionary.

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Study of the Mixture, before Combination. — Now, if some iron filings and pulverized sulphur are stirred together in a mortar, the result is *a mixture.* True, the color is not that of either substance, but with a lens particles of both substances can be seen. Passing a magnet over the mixture will easily remove a part of the iron, and with the help of a lens and a needle the mixture can be picked apart particle by particle, completely. We can **separate** the *components* of the mixture more expeditiously, however, **by using** manipulations based upon certain **suitable properties.** Thus, sulphur dissolves in carbon disulphide while iron does not. If, therefore, a part of the mixture is placed in a dry test-tube along with some carbon disulphide and is shaken, the liquid dissolves the sulphur and leaves the iron. To complete the separation, the iron must be removed from the liquid by filtration, and the sulphur recovered by evaporation of the carbon disulphide.
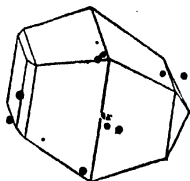
Fig. 7.

Filtration. — Iron, or any solid, when it is mixed with a liquid or with a solution (like the solution of sulphur in carbon disulphide) is said to be **suspended** in the liquid. If the solid is one that settles rapidly, the liquid may be separated from the solid, in a rough way, by pouring off as much of the clear, supernatant liquid as possible. This is called **decantation.**

A complete separation is effected by pouring the mixture on to a cone of filter paper supported in a glass funnel (Fig. 8). The liquid, together with anything that may be dissolved in it, runs through the pores of the paper and down the hollow stem of the funnel. The liquid is then called the **filtrate.** The particles of the suspended solid are too large to pass through the pores, and so collect on the surface of the filter paper.
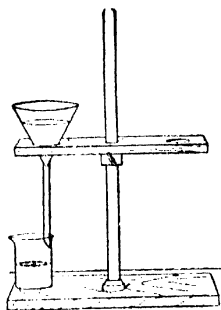
Fig. 8.

This operation, like everything the chemist does, takes advan-
tage of differences in the physical properties of the various
materials

The material remaining on the paper (the residue), when dry,
is wholly attracted by a magnet and shows all the other properties
of iron.

Evaporation. — To recover the sulphur, the solution in carbon
disulphide — the filtrate — is poured into a porcelain evaporat-
ing dish (Carbon disulphide is very inflammable. Keep flames
away!). When the vessel is set aside, the liquid gradually
passes off in vapor (e-vapor-ates). Sulphur, however, does not
evaporate at room temperature and re-
mains as a residue, in the form of crys-
tals of rhombic outline in the bot-
tom of the dish (Fig. 9). Here, again,
differences in physical properties have
been utilized.

FIG. 9.

Since the physical properties of two substances are not
changed by mixing, we have thus used the properties of the
iron and sulphur so as to separate them once more. The iron
is on the paper; the sulphur is in the dish.

Combination of Iron and Sulphur. — But iron and sulphur
are capable of combining to form an entirely new substance, if
we alter the conditions by raising the temperature. When we
place some of the original mixture of iron and sulphur into a
clean test-tube and warm it, we soon notice a rather violent
development of heat taking place, the contents begin to glow,
and what appears to be a form of combustion spreads through
the mass. The heating employed at the start falls far short
of accounting for the much greater heat produced. When these
phenomena have ceased, and the test-tube has been allowed
to cool, we find that it now contains a somewhat porous-looking,
black solid. This material is brittle; it is not magnetic; it does
not dissolve in carbon disulphide; and close examination, even
under a microscope, does not reveal the presence of different kinds
of matter. This substance is known to chemists as ferrous

sulphide and, as we see, its properties are entirely different from those of its constituents.

In this connection we must not omit to notice that, as in rusting, a certain fixed proportion will be used in forming the compound. We find that, for 100 parts of iron, 57.4 parts by weight of sulphur are required. If more iron is put into the original mixture, then some unused iron will be found in the mass after the action. If too much sulphur is employed, some may be driven off as vapor by the heat and any that remains, beyond the correct proportion, can be dissolved out of the ferrous sulphide with carbon disulphide. The sulphur which has combined with the iron, however, is no longer present as sulphur — it has no longer the properties of sulphur, and therefore cannot be dissolved out:

Iron (55.84) + Sulphur (32.06) → Ferrous sulphide (87.90).
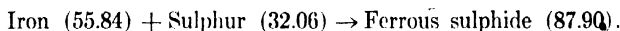
Another Illustration: Mercuric Oxide. — It has already been demonstrated (p. 10) that air contains an active and an inactive gas. A pure specimen of the *active* gas (later to be named oxygen) was first obtained in 1774 by Priestley from mercuric oxide, a bright red, rather heavy powder. When this substance is heated (Fig. 10), we find that a gas is given off. This gas is easily shown to be different from air, since a glowing splinter of wood is instantly relighted on being immersed in it. The gas is pure **oxygen.** During the heating, we notice also that a metallic coating appears on the sides of the tube, in the form of a sort of mirror. Apparently

FIG. 10.

the vapor of some metal is coming off with the oxygen and condensing on the cool parts of the tube. As this shining substance accumulates it takes the form of globules, which may be scraped together. It is, in fact, the metal **mercury,** or quicksilver. If the heating continues long enough, the whole of the red powder eventually disappears, and is converted into these two products.
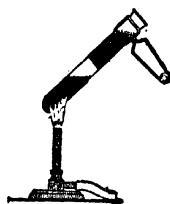
Second Variety of Chemical Change: Decomposition. — Priestley's experiment introduces to us a second, and very com-

mon kind of chemical action. The first variety was combination or union (p. 11). The second is called **decomposition.** It consists in starting with **a single substance** (here mercuric oxide) and **splitting it into two (or more) substances,** which differ in properties from the substance taken and from one another. Here, the red powder gave mercury, a liquid metal, and oxygen, a colorless gas.

Simple and Compound Substances. — We have seen that two (or more) substances, like lead and oxygen, can combine to form a compound substance. Are all substances, then, compounds? We find that some are not. We have never succeeded in obtaining lead, or oxygen, or iron, or tin, or sulphur by combining any two substances. We can decompose mercuric oxide by heat, and we have other ways of decomposing compounds like oxide of tin and ferrous sulphide, but we have never succeeded in decomposing the mercury or the oxygen, the iron or the sulphur themselves. **Substances which we are not able, by chemical means, to decompose into, or to make by chemical union from, other substances** are called **simple substances or elements.** The distinction between simple and compound substances was first drawn by Boyle in 1678. Later, and independently, it was stated very clearly by Lavoisier (1789).

Several substances, regarded in Lavoisier's time as elementary, have since been shown to be compounds. Thus, quicklime was thought to be a simple substance until Davy, in 1808, prepared the metal calcium and showed that quicklime was the oxide of this metal. Hence, we do not say that the substances regarded as simple *cannot* be decomposed, but only that they are substances which we "are not able" (at present) to decompose. We have, nevertheless, as will be seen in a subsequent chapter, so developed in recent years our knowledge of that part of chemistry which deals with the ultimate structure of matter that it is quite inconceivable that any such error as was made in the case of quicklime can recur in the future.

The phrase "**by chemical means**" is very important. Although by ordinary chemical reactions we are not able to effect any decomposition of the elements, yet we cannot regard them as

LAVOISIER ARRESTED BY THE REVOLUTIONISTS

See, page xi

absolutely unalterable and permanent. The rare element *radium* cannot be decomposed by chemical means, but it undergoes continuous and *spontaneous* "disintegration" into the elements *helium* and *lead* (see p 723). The phrase "at will" was until lately employed in place of "by chemical means" in the definition of the term element to care for changes of this type, which we can neither hasten, retard, nor stop by any variation in conditions, but it has been discovered recently by Rutherford that certain common elements, such as *nitrogen* and *aluminium*, may be disrupted at the will of the experimenter with formation of *hydrogen*, by exposing them to the action of the swiftly-moving helium particles ejected from radium in the course of its disintegration. Such phenomena, however, need not affect our conception of elements as applied to every-day chemical reactions, and within the scope of the present volume the defini-tion of the word element given above is sufficient.

Elements. — The word element is used in two senses. It is applied to the simple substance. Thus we speak of "the element iron," meaning the metal iron. It is applied also to the iron-matter contained in ferrous sulphide or in ferric oxide. The reader should note that it is correct usage to speak of the *element* iron and the *element* sulphur in ferrous sulphide, but a chemist would never say that this compound contained the *simple substances* iron and sulphur. If he did, we should understand him to mean that it was a mixture, and we should expect parts of the material to be magnetic like iron, and other parts to be yellow and soluble in carbon disulphide, which is not the case. In the same way the *name* of an element (such as iron) is applied both to the material in combination and to the free substance. Thus "iron" may mean free, uncombined, metallic iron, or iron-matter in some compound. The sense in which the word is employed must be inferred from the context or circumstances. When a chemist speaks, as he sometimes does, colloquially, of "iron" in a drinking water, for example, we know at once that he refers to iron in the form of some compound, for metallic iron does not dissolve in water and, if it did, would quickly turn into rust or some other form of combination.

The word element, then, means one of the simple forms of matter, either free or in combination.

In formally describing a body or specimen, the chemist always avoids the ambiguity just referred to by naming the components, i.e., the substance or substances it contains. He assumes that the nature and constituents of these substances will be known to anyone hearing or reading the description. If he says the body contains zinc and sulphur, it is understood that the body is a mixture of these simple substances. If it contained these elements in combination, the chemist would report that it was sulphide of zinc.

The Common Elements. — Hundreds of thousands of different compound substances are known but, when they are decomposed, it is found that the number of different elements contained in them is not great. Dozens of substances contain iron, hundreds contain sulphur, thousands contain oxygen. In fact, by the combination of a limited number of simple substances, such as carbon, hydrogen, and oxygen, in different proportions by weight, an almost unlimited number of different compound substances may be produced.

A list of all the known elements appears on the inside of the cover, at the end of this book, and contains over eighty names. Of these, a large number are rare, and seldom encountered. More than 99 per cent of terrestrial material is made up of eighteen or twenty elements and their compounds. Only about twenty elements occur in nature in their simple, uncombined condition. Three-fourths of the whole number are found in combination exclusively, and must be liberated by some chemical action.

Taking the atmosphere, all terrestrial waters, and the earth's crust, so far as it has been examined, F. W. Clarke has estimated the plentifulness of the various elements. The first twelve, with the quantity of each contained in one hundred parts of terrestrial matter, and constituting together 99 per cent, are as follows:

Oxygen	. . .	49.85	Calcium . . . 3.18	Hydrogen	. .	0.97
Silicon	. . .	26.03	Sodium . . . 2.33	Titanium	. .	0.41
Aluminium	.	7.28	Potassium . . 2.33	Chlorine	. . .	0.20
Iron	. . . .	4.12	Magnesium . . 2.11	Carbon	. . .	0.19

Thus oxygen accounts for nearly one-half of the whole mass. Silicon, the oxide of which when pure is quartz and in less pure

form constitutes ordinary sand, makes up half of the remainder. Valuable and useful elements, like gold, silver, sulphur, and mercury, are among the less plentiful which, all taken together, furnish the remaining one per cent.

It is convenient in chemistry to divide the elements into two classes — metals and non-metals. The ordinary distinction of physical appearance (metallic luster) is usually valid; thus iron and copper are typical metals, sulphur and oxygen are typical non-metals. A more exact basis for drawing the line between the two classes, however, will be discussed later (pp. 83-84).

Law of Definite Proportions. — In the decomposition of mercuric oxide (p. 19) we find that, for every 100 parts of mercury liberated, 7.97 parts of oxygen by weight are set free. Using the numbers commonly employed in chemistry, which represent the same proportion by weight, we obtain:

Mercuric oxide (216.6) → Mercury (200.6) + Oxygen (16).
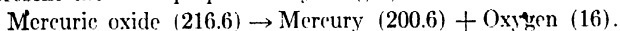
We find also that mercury and oxygen can be made to combine to form mercuric oxide, and the proportions by weight required are the same. Moreover, every sample of mercuric oxide, whether made by combination, or in any of the other possible ways, always contains this proportion of the two elements. We have already seen that the oxides of lead and tin contain fixed proportions (p. 12) of the metal and oxygen and that ferrous sulphide has a constant composition by weight. The same principle is found to apply to all ordinary chemical compounds, and is stated in the **law of definite or constant proportions: In every sample of any compound substance, formed or decomposed, the proportion by weight of the constituent elements is always the same.**

No exception to this law was known until 1914, when it was discovered that lead derived from radio-active disintegrations (compare p. 21) entered into compounds, such as lead chloride, in slightly different proportions by weight than did ordinary lead. A number of other elements have even more recently been shown to exist in two or more forms (*isotopes*), which would, if separable, give compounds possessing the same specific properties yet differing in composition. Detailed discussion of these points

must be deferred to a later chapter (pp. 727-728).‧For all *practical* purposes, the law of definite proportions is still universally valid.

Conservation of Mass. — The most painstaking chemical work seems to show that, if all the substances concerned in a chemical change are weighed before and after the change, there is no evidence of any alteration in the *quantity of matter*. The two weights, representing the sums of the constituents and of the products, respectively, are, indeed, never absolutely identical, but
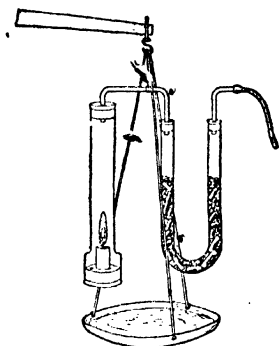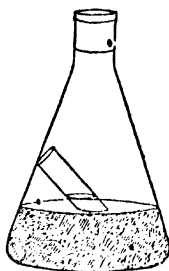
F'IG. 11.   F'IG. 12.

the more careful the work and the more delicate the instrument used in weighing, the more nearly do the values approach identity. We are able to state, therefore, that **the mass of a system is not affected by any chemical change within the system.**

This statement simply means that the great law of the con- servation of mass holds true in chemistry as it does in physics. Chemical changes, thoroughgoing as they are in respect to all other qualities, do not affect the mass; an element carries with it its weight, entirely unchanged, through the most complicated chemical transformations.

Superficial observation, as of a growing tree, might seem to give evidence of the very opposite of conservation of matter. But‧ here the carbon dioxide gas in the air, the most important source of nourishment for plants, is overlooked. Similarly. the gradual

disappearance of a candle by combustion seems to illustrate the destruction of matter. But if we catch *the gases* which rise through the flame (Fig. 11), we find that the gases weigh even more than the part of the candle which has been sacrificed in making them. When we take account of the weight of the oxygen obtained from the air which sustains the combustion, we find that there is really neither loss nor gain in weight. If we carry out chemical changes in closed vessels (Fig. 12), which permit neither escape nor access of material, we find that the weight does not alter.

Physics in Chemistry. — It will be seen that one cannot accomplish anything in chemistry without acquiring and using some knowledge of physics. We measure quantities by means of the physical attributes, weight and volume. We produce chemical change by arranging the physical conditions, for example, by mixing, heating, or using an electric current. Physical means are the only means we possess for producing, stopping, or modifying chemical changes. Again, we ascertain whether a chemical change has taken place or not by observing the physical properties of the materials before and after the experiment. Thus, we noted that the red, powdery oxide of mercury, when heated, gave a liquid metal and a gas. All the phenomena of chemistry are physical. A phenomenon is literally something that is *seen* or, more generally, something that affects any of the senses. Observing physical phenomena is, therefore, our sole means of studying chemical changes. Chemical work is, in fact, entirely dependent upon the skilful use of physical agencies, and upon the close observation of physical phenomena for its success.

It is only the inference, following the experiment and the observation, that is strictly chemical. If one substance gives two different substances, or if two substances give one different substance, for example, we infer that a chemical change has occurred. We then try to recognize the substances by their properties and name them.

• Changes like that of ice into water, or of water into steam, and *vice versa*, are not regarded as chemical changes. These are called **changes of state** (see pp. **74-75**).

Law: Explanation: Scientific Method. — In the preceding pages we have discussed some of the ways that have been invented for classifying the materials and facts included in chemistry. For example, we can prepare many thousand different compound substances and, in the case of *each substance, every specimen* that we have examined contains the same proportions of its constituent elements. So we formulate the law of constant proportions. A **law** or **generalization** in chemistry is a brief statement describing some general fact or constant mode of behavior. Its uses are to condense a great many similar facts into one statement, and thus to make the whole set of facts more easy to remember.

One section in the first chapter (p. 8) was entitled: **"Explanation** of rusting." If that paragraph be now re-read, it will be found that, in the ordinary (as distinct from the scientific) sense of the word, no explanation was given! It has simply been demonstrated that when iron rusts it combines with oxygen from the air. This is an additional fact. It shows *how* iron rusts, namely by taking up oxygen, but not *why* it is able to unite with oxygen. We simply do not know why iron can combine with oxygen gas and platinum cannot.

Explanations in chemistry are of three kinds. (1) We usually try to show that the phenomenon is not an isolated one. Thus, we show that other metals rust. This reconciles us to some extent to the fact that iron rusts, and we feel some mental satisfaction. This is the method of **showing that the fact to be explained is a member of a large class of similar facts.** (2) Next, **we try to get more information about the fact to be explained.** Thus when to the acquaintance with the outward manifestations of rusting, we add the further information that there is an increase in weight, and that this is due to union of oxygen from the air with the iron, we feel increased satisfaction, and say that the fact has been "explained." (3) If we are still dissatisfied, and can discover no further useful facts, **we imagine a state of affairs which, if true, would classify the fact or add to what we know about it.** This step we call explaining by means of an **hypothesis.** We then devote our attention to trying to verify the hypothesis.

The formulation of laws and the making of attempts to ex-

·plain 'facts are part of what is called the **scientific method**. The purpose of this method is to convert the subject matter into a science, that is, into an organized body of knowledge.

Summary. — In this, chapter we have learned: (1) that, while there are many substances, there is a limited number of entirely different kinds of matter (elements) ; (2) that, in addition, to constant physical properties, each substance has a constant composition by weight., We have learned that physical properties are utilized in manipulations, like filtration and evaporation, as well as for identifying substances, and that physical attributes are used for measuring quantities in chemistry and physical conditions for guiding chemical change. Finally, we have seen that a science is not a natural, but a manufactured product, and that the science of chemistry is still in the making.

·Exercises.* — 1. What physical properties are used, (a) in filtration, (b) in evaporation, (c) in the separation and identification of the products from heating mercuric oxide (p 19)?

2. Describe: (a) a red-hot rod of iron, 10 cm. long by 1 cm. diameter, weighing 58.5 g.; (b) a solution of 5 g. of sulphur in 20 c.c. (26 g.) of carbon disulphide at 18° C. In doing so, divide the description into attributes, conditions, and properties.

3. Consider the following materials and state whether, so far as you can now judge, each is a single substance or a mixture: (a) a candle, (b) a cake of soap, (c) an egg.

4. What are the two most direct ways of showing a substance to be a compound? Illustrate each.

5. If we say that quicklime contains calcium (p. 20), do we mean the element or the simple substance calcium?

6. What explanation was given, (a) of the disappearance of mercuric oxide when heated, (b) of the absence of iron and sulphur, as substances, from ferrous sulphide? Which of the three kinds of explanation was used in each case?

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* The exercises should in all cases be studied with minute care. They not only serve as tests to show that the chapter has been understood, but very frequently (as in No. 4) also call attention to ideas which might not be acquired from the text alone, or (as in Nos. 1, 2, 5) assist in elucidating ideas given in the text which, without the exercises, might not be fully grasped.

CHAPTER III

OXYGEN

WE cannot do better than begin the more systematic study of chemistry with oxygen, for it is a most interesting as well as useful substance. We depend upon it for *life*, since in its absence we suffocate, for *heat*, since wood, coal, and gas will not burn without it, and even for *light* where oil, gas, or a candle is used.

We wish to know with which substances we use in the laboratory it can combine, as well as the substances on which it has no action. This information will show us how to work, in future, without interference from the oxygen in the air and whether oxygen has probably played a part in some experiment or not.

Let us take up, then, (1) the history of the element, (2) what materials contain oxygen (occurrence), (3) how we can obtain it in a pure state (preparation), (4) what its specific physical properties as a substance are, and (5) what it does, and what it cannot do in nature and in the laboratory (chemical properties). The classification of the facts about this, and other substances, under five heads is somewhat mechanical, but has the advantage of enabling the reader quickly to find any required information.

History of Oxygen. — Leonardo da Vinci (1452-1519) seems to be the first European to mention the presence of two different gases in atmospheric air. Mayow (1669) measured the proportion of oxygen in the air and discussed fully its uses in combustion, rusting, vinegar-making, and respiration, but did not make a pure sample. Hales (1731) made it from saltpeter, and measured the amount obtainable, but did not see any connection between it and the air! Bayen (Apr., 1774) was the first to make it by heating mercuric oxide. Priestley (Aug. 1, 1774) made it by heating the same substance and quite purposelessly,

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as he admits, thrust a lighted candle into it and was delighted
with the extreme brilliance of the flame. He had, however, en-
tirely incorrect ideas about its nature, and no notion until a year
later that it was a component of the air. Scheele, a Swedish
apothecary, had made it in 1771-2 from no less than seven
different substances and understood clearly that atmospheric
oxygen combined with metals, phosphorus, hydrogen, linseed oil
and many other substances. But the publisher did not get his
book out until 1777, and Priestley is usually credited with the
"discovery" of the element. Finally, Lavoisier (1777) heated
mercury in a retort (Fig. 13), the neck of which projected into a
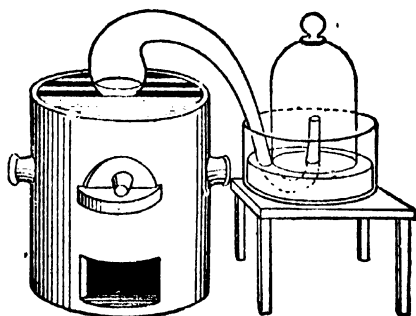
Fig. 13.

jar standing in a larger dish of mercury. The air, thus enclosed
within the jar and the retort, during twelve days lost one-fifth
of its volume. Simultaneously, red particles of mercuric oxide
accumulated on the surface of the mercury in the retort. The
residual gas, nitrogen, no longer supported life or combustion.
The oxide, on being heated more strongly, by itself, gave off a
gas whose volume exactly corresponded with the shrinkage
undergone by the enclosed air, and this gas possessed in an
exaggerated degree the properties which the air had lost. The
proof that oxygen was a component of the atmosphere was
therefore complete. Later, Lavoisier, in the mistaken belief that

the new element was an essential constituent of all sour substances, named it **oxygen** (Greek, *acid-producer*).

Occurrence. — As we have seen, nearly 50 per cent of terrestrial matter is oxygen. Water contains about 89 per cent, the human body over 60 per cent, and common materials like sandstone, limestone, brick, and mortar more than 50 per cent of this element. One-fifth by volume (nearly one-fourth by weight) of the air is free oxygen.

Preparation of Oxygen. — 1. The oxygen of commerce is now made chiefly from liquefied air (p. 374). This consists essentially of a mixture of liquid oxygen and liquid nitrogen. Now pure liquid oxygen boils at − 182.5°, but pure liquid nitrogen boils at an even lower temperature (− 194°). Consequently, when liquid air is allowed to evaporate slowly, the nitrogen boils off much more freely than does the oxygen. After a time, when the remaining liquid is almost pure oxygen (96 per cent), the gas coming off is compressed by pumps into the steel cylinders (Fig. 14) in which it is sold. In medicine, patients suffering from pneumonia or suffocation obtain some relief by inhaling it in this form. It is also used in feeding flames, instead of air, when intense heat is required (see acetylene torch and calcium light).
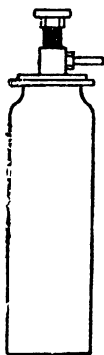
FIG. 14.

2. Unfortunately, it is difficult to liberate oxygen from **natural substances.** Saltpeter (potassium nitrate), for example, which is found in many soils and can be dissolved out with water, gives off oxygen only when raised to a bright red heat by the Bunsen flame or blast lamp, and even then it gives up only one-third of the **oxygen** it contains (202.2 g. give 32 g. of oxygen).

3. In practice, we are compelled to use manufactured substances. „Amongst the artificial substances are mercuric oxide, expensive but historically interesting (p. 19), potassium chlorate, perhaps the most convenient for laboratory use, and sodium peroxide. **Potassium chlorate** is a white crystalline substance used, on account of the

oxygen it contains, in large quantities in the manufacture of matches and fireworks. When heated in a tube similar to that in Fig. 10, it first melts (357°) and then, on being more strongly heated, it effervesces and gives off a very large volume of oxygen. Examination shows that the whole of the oxygen it contains (39 per cent) can be driven out. The white material which remains after the heating is identical with the mineral sylvite, To the chemist it is known as potassium chloride. The change, together with the weights of the materials, is as follows:

Potassium chlorate (122.56)→Potassium chloride (74.56) + Oxygen (48)

Potassium (39.1)   Potassium (39.1)
Chlorine (35.46)   Chlorine (35.46)
Oxygen (48)
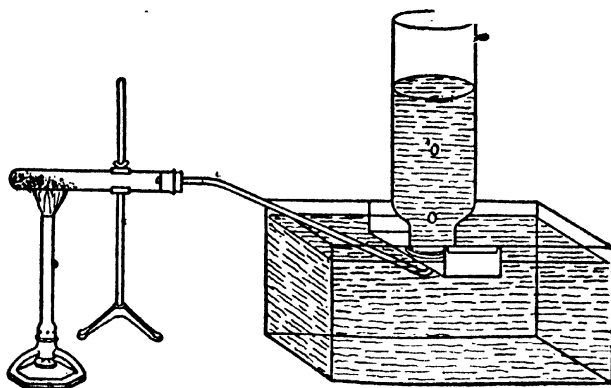
FIG. 15.

A peculiarity of this action is that admixture of manganese dioxide (the mineral pyrolusite) increases very markedly the speed with which the decomposition of the potassium chlorate takes place. Hence powdered manganese dioxide is generally mixed with the chlorate in laboratory experiments (Fig. 15), and in its presence a sufficient stream of the gas is obtained at a relatively low temperature (below 200°).

4. Oxygen can be obtained conveniently from **sodium peroxide** and water by means of generators (Fig. 16) similar to the acety-

lene generators used on automobiles. When the metal sodium is
burned in air, sodium peroxide is obtained as a powder. This

powder, after being melted, solidifies in
compact, solid form, and is sold as **oxone**.
The oxone is bought in a small, sealed
tin can, the ends of which are perforated
in several places just before use. When
the valve (B) is opened, the water, which
fills the generator almost to the top,
enters the can (C) by the holes in the
bottom and interacts with the oxone
forming sodium hydroxide and oxygen.
The sodium hydroxide produced is very
soluble in water and remains dissolved;
the oxygen escapes through the valve.
When the valve is shut, the gas continues
to be generated until it has driven the
water down again below the level of the
bottom of the can.

FIG. 16.

Sodium peroxide(156)+Water(36)→Sodium hydroxide(160)+Oxygen (32)

Sodium (92)	Hydrogen (4)	Sodium (92)	
Oxygen (64)	Oxygen (32)	Oxygen (64)	
		Hydrogen (4)	

This method is convenient because it works at room temperature
and can be started and stopped at will.

Catalytic or Contact Action. — The influence of manganese
dioxide in causing the potassium chlorate to decompose more
easily (p. 31) well deserves notice. The effect is very striking if
some pure potassium chlorate is melted carefully, to avoid super-
heating, in a wide-mouth flask (Fig. 17). The flask is provided
with a wide exit tube, from which a rubber tube may lead to a
bottle inverted in a trough filled with water as in Fig. 15. A
little manganese dioxide is contained in the upper, closed tube.
No effervescence of the chlorate can be seen at its melting-point
(357°) — only a little air, expanded by the heating, issues from
the tube. When, however, the closed tube containing the man-
ganese dioxide is rotated into a vertical position (see dotted

• lines}, and the black powder falls into the chlorate, the oxygen comes off in torrents, in consequence of the enormous acceleration of the decomposition. As a pre-
caution against injury from an
explosion, it is advisable to
wrap the flask in a towel be-
fore turning the tube.   •

It must also be noted that
the manganese dioxide is not it-
self permanently altered. If
the material left after the ac-
tion is shaken with water, the
potassium chloride dissolves,
while the dioxide does not.
Filtration (p. 17) then enables
us to recover the latter, and to
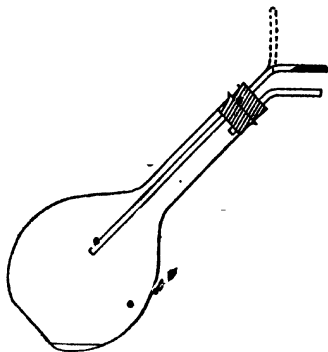
Fig. 17.

ascertain that it has been changed neither in quantity nor in properties.

The only effect of the dioxide is to *hasten* the decomposition of the chlorate, which would otherwise be too slow at 200° (p. 31), or even at 357° (its m.-p.) to be of any practical value. **Substances which hasten a chemical action without themselves undergoing any permanent change** are called **contact agents, catalytic agents, or catalysts.** The process is called **contact action or catalysis** (Greek, *decomposition*, not a very fortunate choice of words). Such substances are frequently used in chemistry. The addition of a suitable catalyst is one of the *conditions* (p. 7) for carrying out actions in which a contact agent is necessary. Many substances of this class are secreted by animals and plants and play an important part in digestion, fermentation, and other physiological changes. Their presence often enables very complex chemical actions to proceed rapidly at rather low temperatures.

The oxone, mentioned above, always contains a catalyst, a trace of cuprous oxide, which hastens the action on water.

• Specific Properties of Two Kinds, Physical and Chemical. — We have learned that every substance has its own set of specific properties. In describing a substance, it is convenient to

divide the properties into two classes. The list of substances with which the given substance can enter into chemical combination for example, we place under **specific chemical properties**. Relations of the substance to any of the varieties of chemical change belong to this class.

On the other hand, we do not consider melting or boiling to be chemical changes, so we place the temperatures at which the substance melts (m.-p.) and boils (b.-p.), its color, etc. (for list, see pp. 6-7), under **specific physical properties**.

Properties of either class may be used for recognizing a substance.

Specific Physical Properties of Oxygen. — Oxygen resembles air in having neither *color, taste,* nor *odor.* The *density* of a substance is, strictly speaking, the weight in grams of 1 cubic centimeter. In the case of a gas, we frequently prefer to give the weight of 1000 c.c. (1 liter), at 0° and 760 mm. (1 atmosphere) barometric pressure. For oxygen this weight is 1.42900 grams (Morley). The corresponding weight for air is 1.293 g., so that oxygen is slightly heavier, bulk for bulk, than air (in the ratio 1.105 : 1). It is much heavier than hydrogen, however, since one liter of this gas under the above conditions weighs only 0.08987 grams. Oxygen can be *liquefied* by compression, provided its temperature is first reduced below – 118°, which is its critical temperature.* The gas is only slightly *soluble* in *water* under atmospheric pressure, the solubility at 0° being 4.9 volumes of gas in 100 volumes of water (at 20°, 3.1 : 100).

The solubility of oxygen in water, although slight, is in some respects its most important physical property. Fish obtain oxygen for their blood from that *dissolved in* the water. With air-breathing animals (like man), the oxygen could not be so readily taken into the system, if it did not first dissolve in the moisture contained in the walls of the air sacs of the lungs, and then pass inwards in a dissolved state to the blood.

Liquid oxygen, first prepared by Wroblevski, has a pale-blue

Each gas has an individual critical temperature (p. 55) above which no pressure, however great, will produce liquefaction. The farther the temperature of a specimen of the gas is below the critical point, the less will be the pressure required to liquefy it.

color. At one atmosphere pressure, that is, in an open vessel, it boils at — 182.5°. Its density (weight of 1 c.c.) is 1.13, so that it is slightly denser than water. By cooling with a jet of liquid hydrogen, Dewar froze the liquid to a snow-like, pale-blue solid. A tube of liquid oxygen is noticeably attracted by a magnet.

Six Specific Physical Properties of Each Gas. — Although every substance has many physical properties, we shall mention only those which are used in chemical work, with occasionally the addition of any peculiar or unexpected quality. It will aid the memory to recall the physical properties of a *gas*, if we note that, as a rule, only *six* such properties are mentioned: (1) color, (2) taste, (3) odor, (4) density, (5) liquefiability, defined by the critical temperature, (6) solubility, usually in water only.

Specific Chemical Properties of Oxygen. — The chemical properties of pure oxygen are like those of atmospheric air, only more pronounced.

FIG. 18.

Reactions with Non-metallic Elements. Sulphur, when raised in advance to the temperature necessary to start the action, unites vigorously with oxygen (Fig. 18), giving out much heat and producing a familiar gas having a pungent odor (sulphur dioxide). This odor is frequently spoken of as the "smell of sulphur," but in reality sulphur itself has no odor, and neither has oxygen. The odor is a property of the compound of the two. The mode of experimentation can be changed and the oxygen led into sulphur vapor through a tube. The oxygen then appears to burn with a bright flame, giving the same product as before.

Phosphorus, when set on fire, blazes in oxygen very vigorously, forming a white, powdery, solid oxide — phosphorus pentoxide. Burning *carbon,* in the form of charcoal or hard coal, glows brilliantly and is soon burnt up. It leaves an invisible, odorless gas
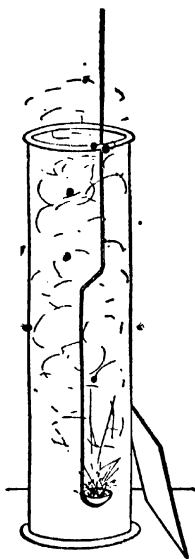
— carbon dioxide. A stream of *hydrogen* burns with a very hot flame in oxygen, producing *steam*, which condenses on the cooler walls of the containing vessel as droplets of liquid *water*. At high temperatures, oxygen combines readily with one or two other non-metals (*e.g.*, silicon, boron, and arsenic), and to a small extent (1 per cent at 1900°) with nitrogen. It will not combine directly with chlorine, bromine, or iodine, although oxides of the first and last can be prepared by using other varieties of chemical change. With the six members of the helium family (p. 376), of which no compounds are known, and with fluorine, oxygen forms no compounds.

Sulphur (32.06) + Oxygen (32) → Sulphur dioxide (64.06).
Phosphorus (124.16) + Oxygen (160) → Phosphorus pentoxide
(284.16).
Carbon (12.005) + Oxygen (32) → Carbon dioxide (44.005).
Hydrogen (4.032) + Oxygen (32) → Water (36.032).

Reactions with Metallic Elements. Iron, as we have seen (p. 9), rusts exceedingly slowly in air and, even when red-hot, gives hammer-scale, the black solid which is broken off on the anvil, rather deliberately. In pure oxygen, however, iron in the form of picture-wire, if once ignited, will burn with surprising brilliancy, throwing off sparkling globules of the oxide, melted by the heat. This oxide is a black, brittle substance, identical with hammer-scale, and different from rust (ferric oxide). It contains, in fact, a smaller proportion of oxygen than does the latter, and is called magnetic oxide of iron.

Iron (167.52) + Oxygen (64) → Magnetic oxide of iron (231.52).

All the familiar metals, excepting gold, silver, and platinum, when heated, combine with oxygen, some more vigorously, others less vigorously than does iron. Oxides of the three metals just named can also be made, but only by varieties of chemical change other than direct combination.

Compound substances, if they are composed largely or entirely of elements which combine with oxygen, are generally able them-selves to interact with oxygen. Usually, they produce a mixture of the same oxides which each element, separately, would give.

Hence wood, which is composed of carbon and hydrogen with some oxygen, when burnt in oxygen, produces carbon dioxide and water (oxide of hydrogen) in the form of vapor. Again, carbon disulphide burns readily, giving carbon dioxide and sulphur dioxide, just as do carbon and sulphur, separately. Ferrous sulphide gives, similarly, sulphur dioxide and magnetic oxide of iron.

Tests. A Test for Oxygen. — A test is a property which, because it is easily recognized (a strong color, for example), or because it is especially distinctive, **is commonly employed in recognizing a substance.**

Oxygen, as we have seen (p. 19), *when pure,* is recognized by the fact that a splinter of wood, glowing at one end, bursts into flame when introduced into the gas. Only one other gas (see nitrous oxide) behaves similarly.

The Measurement of Combining Proportions. — In a number of condensed statements we have given the proportions by weight of the materials combining. It is now desirable that we should know how the necessary measurements are made. The most exact measurement of the proportions in which the elements combine to form compounds involves manipulations too elaborate to be gone into here. One or two brief statements, diagrammatic rather than accurate, will show the principles, however.

If we take a weighed quantity of iron in a test-tube and heat it with more than enough sulphur (an **excess** of sulphur), we get free sulphur along with the ferrous sulphide (p. 19), and no free iron survives. We may remove the free sulphur by washing the solid with carbon disulphide. The difference between the weights of the ferrous sulphide and the iron gives the amount of sulphur combined with the known quantity of the latter.

As an example of the study of the combination of a metal with oxygen, we may weigh a small amount of copper in the form of powder in a porcelain boat and pass oxygen over the heated metal until it is completely converted into black cupric oxide (Fig. 19). The original weight of the copper, and the increase in weight, representing oxygen, give us then the data for determining the composition of this oxide. The data furnished by one rough lecture-experiment, for example, were as follows:
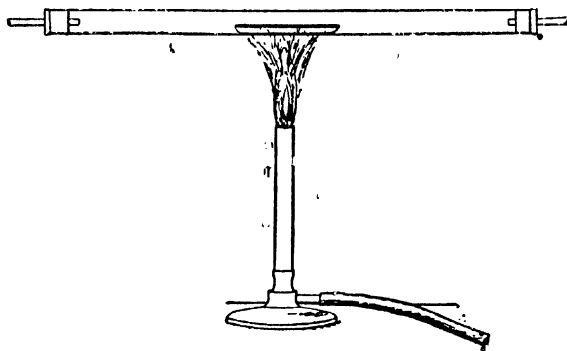
Fig. 19.

Weight of boat + copper . . . . 4.278 g.
Weight of boat empty . . . . 3.428 g.

Difference — weight of copper . . . . 0.850 g.

Weight after addition of oxygen . . . . 4.488 g.
Weight without oxygen . . . . 4.278 g.

Difference = weight of oxygen . . . . 0.210 g.

The proportion of copper to oxygen, so far as this one measurement goes, is therefore 85 : 21.

The results of quantitative experiments are often recorded in the form of parts in one hundred. To find the percentage of each constituent, we observe that the proportion of copper is 85 : 85 + 21, or $^{85}/_{106}$ of the whole. That of the oxygen is $^{21}/_{106}$ of the whole. Thus the percentages are:

Copper, 106 : 85 :: 100 : x.   x = 80.2.
Oxygen, 106 : 21 :: 100 : x'.   x' = 19.8.

Naturally, the mean of the results of a number of more carefully managed experiments will be nearer the true proportion. The percentages at present accepted as most accurate are 79.9 and 20.1.

In the case of mercuric oxide, we may decompose a known

weight of the oxide (p. 23), collect the mercury and weigh it, and ascertain the oxygen by difference.

The names of the constituent elements in a compound, together with the proportions by weight in which they are present, are called the **composition** of the substance. For practical purposes, *percentage compositions* are often used. Thus, the *percentage composition* of cupric oxide is copper : oxygen :: 79.9 : 20.1, as we have seen above. However, another set of numbers expressing the same proportion (63.57 : 16) is more frequently employed in chemistry, for reasons which will be developed later.

All **experiments involving measurement,** such as those used in determining composition, are called **quantitative experiments.**

Another Quantitative Experiment. — The following will show how the combining proportions may be measured when the product is a gas, the weight of which must be ascertained. Sul- phur burns in oxygen to form sulphur dioxide. A known weight
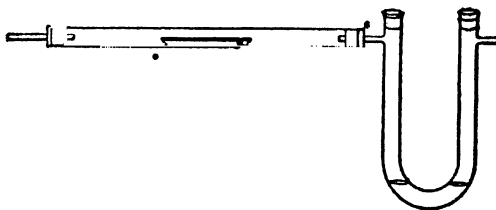
FIG. 20.

of sulphur is placed in a porcelain boat (Fig. 20), which has already been weighed. The U-shaped tube to the right contains a solution of potassium hydroxide, which is capable of absorbing the resulting gas. The oxygen enters from the left. When the sulphur is heated, it burns in the oxygen, and the gain in weight of the U-tube shows the weight of the compound produced. By subtracting from this the weight of the sulphur taken, we get the quantity of oxygen with which it has combined.

In one experiment, the weight of the sulphur taken was 1.21 g. The weight gained by the U-tube was 2.42 g. The difference (= oxygen) is 1.21. The proportion of sulphur to oxygen in sulphur dioxide is therefore 1.21 : 1.21 or 1 : 1 or, in percentages,

50 : 50. This proportion is very close to the accepted value (p. 36), 32.06 : 32.

The same method could be used for carbon, for the carbon dioxide produced would be absorbed in the solution of potassium hydroxide.

Combustion. — Violent union with oxygen is called, in popular language, **combustion** or burning. Yet, since similar vigorous interactions with other gases are common, the term has no special scientific significance. Even the union of iron and sulphur gives out light and heat, and is quite similar in the chemical point of view to combustion.

A misleading term often used in this connection is **kindling temperature.** It gives the impression that there is a definite temperature at which combustion will start. But the temperature is only *one* of the conditions which produce combustion. Finely powdered iron will start burning at a lower temperature than will an iron wire, *because it presents relatively more surface to the gas.* Again, if the oxygen is at less than one atmosphere pressure, the wire will require to reach a higher temperature before combustion will begin. Finally, the vapor of methyl alcohol and air requires to be raised above a red heat before combustion starts, but a pocket cigar-lighter sets fire to this very mixture by means of a contact agent (a thin platinum wire) without any other means of heating being required. So that the conditions under which combustion begins involve the physical condition of the solid, the pressure of the gas or vapor, the presence or absence of a contact agent and the nature of the contact agent, as well as the temperature. No definite kindling temperature can be given, unless the other conditions are specified also. Kindling conditions involve several variables, of which the temperature is only one.

Oxidation. — The slower union with oxygen which occurs in rusting is called **oxidation.** We shall see later, however, that it has been found convenient to stretch this term so as to cover combinations of other elements than oxygen, and even to include actions not involving combination. At this point we can discuss only oxidation by oxygen.

This process of slow oxidation by oxygen, although less conspicuous than combustion, is really of greater interest. Thus the decay of wood is simply a process of oxidation whereby the same products are formed as by the more rapid ordinary combustion. Sewage is mixed with large volumes of river water, the object being, not simply to dilute the sewage, but to mix it with water containing oxygen in solution. This has an oxidizing power like that of oxygen gas and, through the agency of bacteria, quickly renders dissolved organic matters innocuous by converting them for the most part into carbon dioxide and water. Thus, a few miles farther down the stream, the water may become as suitable for drinking as it was before the sewage entered. In our own bodies we have likewise a familiar illustration of slow oxidation. Avoiding details, it is sufficient to say that the oxygen, from the air taken into the lungs, combines with the hæmoglobin in the red blood-corpuscles. In this form of loose combination, it is carried by the blood throughout our tissues and there oxidizes the food-stuffs which have been absorbed during digestion. The material products are carbon dioxide and water, of which the former is carried back to the lungs by the blood, and finally reaches the air during exhalation. The important product, however, is the heat, given out by the oxidation, which keeps the body warm.

The opposite of oxidation, the *removal* of oxygen, is spoken of in chemistry as **reduction**. But this term, also, has been stretched to cover other kinds of chemical change.

Spontaneous Combustion. — Sometimes a mere slow oxidation develops into a combustion, which is then known as **spontaneous combustion.** To understand this, we must note the fact that a given weight of material, say iron, in combining with oxygen to form a given oxide, will liberate the same total amount of heat whether the union proceeds rapidly or slowly. If the action proceeds slowly, and the material being oxidized is freely exposed to the air, the latter will become heated and will carry off the heat as fast as it is produced. Thus, no particular rise in temperature will occur. If, however, the material is a poor conductor of heat, like hay or rags, and there is sufficient air for oxidation, but not enough to carry off the heated air, the heat

may accumulate and a temperature sufficient to start combustion may be reached. Such a situation sometimes arises in hay-stacks. It occurs also when rags, saturated with oil used in making paints (linseed oil and turpentine) are left in a heap. These oils, in "drying," combine with oxygen from the air and turn into a tough, resinous material. The rags, being poor conductors of heat, finally become hot enough to burst into flame, and serious conflagrations often owe their origin to causes such as this. Oily rags should always be disposed of by burning, or should at least be placed in a closed can of metal. Fires in coal bunkers of ships arise from the same cause — slow oxidation, with accumulation of the resulting heat. That coal does undergo slow oxidation, especially when freshly mined, is shown by the fact that such coal, if left exposed to the air for months, may lose 10 per cent or more of its heating power.

Uses of Oxygen. — In the foregoing sections we have referred to its use in breathing, its rôle in decay, which is a beneficent process because it removes much useless matter which might otherwise cause disease, and its value in the disposal of sewage. Power and heat for commercial purposes are almost all obtained by the burning of coal, in which oxygen from the air plays a large part. If we had to purchase the oxygen as well as the coal, we should require at least three tons of oxygen for every ton of coal.

Oxygen in cylinders and oxygen generators are used to restore the supply in the atmosphere of submarine boats, and to assist the respiration of aviators at very great altitudes.

Substances Indifferent to Oxygen. — Finally, since the atmosphere contains so large a proportion of oxygen, substances which do *not* oxidize and, when heated, do *not* burn, have many uses. Gold, silver, and platinum are of this kind (p. 36), and are used for ornaments. The last is used for crucibles in which bodies are heated in the laboratory. Although iron burns in pure oxygen, it does not oxidize rapidly in the air even when heated, and so is used for making vessels for cooking and in constructing fireproof buildings.

Substances, already fully oxidized, are naturally not combustible. Of this nature are sandstone, granite, brick, porcelain, glass, and water. All these are, therefore, fireproof. Moreover, these substances do not give off oxygen when heated. It is this *inactivity* which renders glass and porcelain suitable materials for laboratory apparatus, since they experience no change in weight when heated.

Activity and Stability. — A substance which enters into combination vigorously, as does oxygen, is called chemically **active.** Nitrogen, on the other hand, is relatively **inactive.** An active element, since it combines readily, also holds tenaciously to the matter with which it has combined. An active element implies, therefore, one which is in general difficult to liberate from combination. Its compounds are in general relatively **stable** or **inactive.** Thus, many oxides, and the natural compounds just mentioned (sandstone, granite, brick and porcelain, the last two made from clay), do not lose oxygen even at a white heat and are very *stable.* The compounds of more indifferent elements, on the other hand, are in general relatively easy to decompose. In other words, they are **unstable or active.**

Exercises. — 1. What percentage by weight of free oxygen is obtained by heating: (a) mercuric oxide, (b) potassium nitrate, (c) potassium chlorate? At $1.50, $0.15, and $0.15 per kilogram, respectively, which is the cheapest source of oxygen?

2. Using the data on p. 34, calculate the weight of oxygen dissolved by 1000 c.c. of water at 0° under one atmosphere pressure.

3. Why does a forced draft make a fire burn more rapidly?

4. Why does a naked flame sometimes cause an explosion in a mine, when the air of the mine is filled with coal dust?

5. The substances, like phosphorus and sulphur, which burn rapidly in ordinary oxygen, combine very, very slowly with oxygen which has been freed from moisture by careful drying. How is this effect of water to be classified?

6. Air is 20 per cent oxygen. Why does iron burn brilliantly in pure oxygen, but not in air?

CHAPTER IV

THE MEASUREMENT OF QUANTITY IN GASES. THE KINETIC-MOLECULAR HYPOTHESIS

AFTER the discussion in regard to the proportions of oxygen in the air and the measurement of the volume of oxygen removed (Fig. 6, p. 9), it will readily be imagined that measuring the volume of a sample of gas is a common operation in chemistry. Indeed, it is much easier to measure quantities of gas by noting their volumes than by weighing them. Some facts have to be taken account of, however, in order that the measurements of the volume may be of value.

A sample of gas diminishes in volume when the pressure increases, and it increases in volume when the temperature rises. Hence, when the volume of the gas is measured, the pressure and the temperature must also be stated.
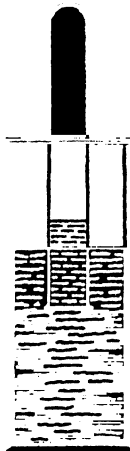
The Measurement of the Pressure of a Gas. — In almost all cases the easiest way to take account of the pressure of a gas is to place it in an apparatus so constructed that one boundary of the volume is a liquid. The apparatus is then so adjusted that the surface of the liquid in contact with the gas in the closed tube (Fig. 21) is *at the same level* as the *free* surface of the liquid which is exposed to the atmosphere. The equality in the levels of the liquids is then a guarantee that the specimen of gas and the atmosphere are exercising equal pressures on the liquid. At this stage the volume of the gas is measured, by reading the graduation (not shown) on the tube. Simultaneously the pressure of the atmosphere and, therefore, of the gas, is ascertained by reading the barometer.

Fig. 21.

44

A simple form of barometer is shown in Fig. 22 (tube on right of diagram only). A glass tube, about 1 meter long and closed at one end, is completely filled with mercury and carefully inverted, with its open end dipping into a mercury reservoir. The mercury falls inside the tube, leaving a vacuum at the top, until the pressure of the mercury column inside balances the pressure of the air outside. The atmospheric pres-
sure is therefore expressed by the barometer as equivalent to the pres-
sure exerted by so many *millimeters of mercury*. For accurate work, all readings obtained must be reduced to a standard temperature (0° C.), by correcting for the expansion of mer-
cury above that temperature.

A more practical form of barom-
eter for laboratory use consists of a bent tube containing mercury (Fig. 22, left half of diagram). The short limb (to the left) is open and the pressure of the atmosphere is exercised on the surface of the mercury there. The longer limb (to the right) is closed at the top and in it there is no gas above the mercury. Hence, reading the difference in the heights at which the mercury stands in the two limbs gives us a measure of the pressure of the atmosphere and of any specimen of gas which is at the same pressure.

FIG. 22.

This is called the *uncorrected* reading. It is immediately re-
duced to the *corrected* reading by noting the temperature on the adjacent thermometer and referring to the table of corrections (C, Fig. 22) supplied with the barometer.

For example: the uncorrected barometric reading is 744 mm. with the barometer at 15°. The correction on 744 mm. at 15°, according to the table, is —2.0 mm. The corrected reading is therefore 742 mm.

• Correction of the Volume to 760 mm. Pressure (Boyle's Law). — Since the atmospheric pressure varies from day to day, the volume of the gas at the observed pressure is next corrected
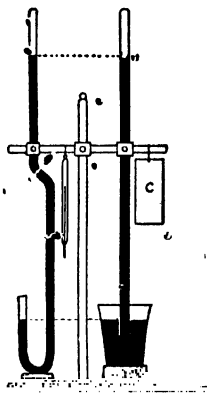
to that which the same quantity of gas would have occupied at the standard pressure of 760 mm. of mercury   By careful measurements, **Boyle** (1660) found that the **volume occupied by the same sample of any gas at constant temperature varies inversely with the pressure.**

An illustration will show how this correction is applied. Let us suppose that there were 100 c.c. of the gas at 15° and 742 mm. (corr.). The question is: What would be the volume of this amount of gas at 760 mm.? At this new pressure (760 mm.), which is *greater* than the old pressure (742 mm.), the volume will become *less*. Hence we change the volume in the proportion of these pressures, *placing the smaller number in the numerator*, so as to get a smaller volume as the answer: $200 \times {}^{742}/_{760} =$ volume at 760 mm. $=$ 195.3 c.c. If we wished to convert 100 c.c. at 775 mm. to 760 mm., we should reason that the new pressure was smaller, and the volume would become greater, and should therefore place the larger number (775) in the numerator so as to get a larger volume for the answer.

The Correction of the Volume of a Gas for Temperature (Charles' Law).

— All gases at 0° C. are found to gain 1 part in 273 of their volume when heated to 1°, 2 parts in 273 when heated to 2°, and so on in proportion, so long as the pressure is maintained constant. Thus at 273°, under constant pressure, the volume is doubled. When cooled below 0°, every gas similarly loses 1 part in 273 of its volume for each degree. At – 273°, if the regular contraction continued so far, the sample would, by calculation at least, lose all its volume. This temperature (the lowest temperature that could possibly be attained) is called the **absolute zero.** In point of fact, however, all gases liquefy before the temperature has fallen to – 273°.

The rule contained in the above statements is known as **Charles' Law.** By applying an arithmetical device, we can state the law in a form which makes its use in calculations quite easy. The device consists in *adding 273 algebraically to all temperatures on the Centigrade scale.* The temperature, when 273 has been added, is called the **absolute temperature.** Charles' Law then reads as follows: **The volumes assumed by a sample of gas**

, at different temperatures, the pressure remaining constant, are directly proportional to the corresponding absolute temperatures.

In the illustration used above, there were 200 c.c. of gas at 15°, and it is required to know the volume at 0°. We *add 273 algebraically to each temperature*, and the question becomes: There are 200 c.c. of gas at 288° Abs., what will be its volume at 273° Abs.? The volume changes in the direct ratio of the absolute temperatures. The new temperature is *lower* than the old, and the new volume will, therefore, be *smaller* than the old. Then $200 \times {}^{273}\!/_{288}$ = volume at 0° (273° Abs.) = 189.6 c.c.

The above laws are usually applied to any example simultaneously. Thus, 200 c.c. of gas at 742 mm. pressure (corr.) and 15° become $200 \times {}^{742}\!/_{760} \times {}^{273}\!/_{288}$ = 185.1 c.c. at 0° and 760 mm.

If a sample of a gas is heated and its *volume is kept constant*, then we find that its *pressure is directly proportional to the absolute temperature*. This is not a third law distinct from that of Boyle and of Charles, but is derived by combining the two.

Mixed Gases (Dalton's Law). — Different gases at the same temperature, provided they do not interact chemically, exert no influence at all upon each other when mixed. Each component of the mixture behaves as if all the others were absent and it alone were in occupation of the whole available volume. Thus if we mix 100 c.c. of oxygen and 100 c.c. of hydrogen, both at one atmosphere pressure, the resultant gas occupies 200 c.c. at this same pressure, but both the oxygen and the hydrogen act as if they were under a pressure of *one-half an atmosphere*. This may be generalized into the law of partial pressures, first formulated by Dalton in 1807: The pressure exercised by each component in a gaseous mixture is proportional to its concentration in the mixture, and the total pressure of the gas is equal to the sum of those of its components.

This law is particularly useful in correcting to standard conditions a given volume of a gas which has been collected over water, since such a specimen necessarily contains water vapor. The partial pressure of this, called aqueous tension (p. 75), which is definite for each temperature, must be subtracted from the

total pressure in order to obtain the partial pressure of the gas being measured, and the remainder must be used as the pressure of this gas in any calculation. Thus, in a gas measured over water at 22°, the total pressure includes 19.7 mm. pressure of water vapor (the aqueous tension at 22°, see Appendix III, p. 734). Hence 150 c.c. of gas over water at 22° and 750 mm. is the same in amount as 150 c.c. of the same gas in dry condition at 22° and 730.3 mm. (there being simply 150 c.c. of water vapor at 19.7 mm. mixed with it). To obtain the volume of dry gas at 0° and 760 mm. we have the expression $150 \times {}^{273}\!\!/_{295} \times {}^{730.3}\!\!/_{760}$.

Densities of Gases. — The density of a gas is the mass of 1 c.c. of the gas at 0° and 760 mm. pressure. Sometimes the weight of one liter (1000 c.c.) is called the density. Often the *relative weight* of the gas, the weight of an equal volume of air, or oxygen, or hydrogen being taken as unity, receives the same name (see p. 34).

Fig. 23.

The most direct method of measuring the density of a gas is to employ a light flask of 125–150 c.c. capacity, provided with a rubber stopper and stop-cock (Fig. 23). By means of an air-pump the con-tents of the flask are removed, and it is weighed. This gives the weight of the empty vessel. The gas, whose density is to be ascertained, is then admitted, and care is taken that it finally fills the flask at the pressure of the atmosphere. The flask is closed and weighed again. The increase represents the weight of the gas. At the same time the temperature and barometric pressure are read. The volume is determined by displacing the gas once more from the flask, filling with water, and weighing again. The difference in weight between the empty flask and the flask full of water, in grams, represents the volume of the content of the flask in cubic centimeters. This volume is reduced to 0° and 760 mm. by the rules discussed above, and we have then a volume of the gas and the corresponding weight.

To illustrate, let us suppose that the volume of the flask is 200 c.c. and that it is filled with oxygen at 15° and 742 mm. The weight of the gas is found to be 0.26 g. We ascertained (p. 47)

by calculation that at 0° and 760 mm. this volume would be 185.1 c.c. The weight of a liter is given by the proportion 185.1 : 0.26 :: 1000 : x. Here $x = 1.405$ g. When the operation is performed carefully, and. the weighing carried to the nearest milligram instead of the nearest centigram, a result more nearly · approaching the accepted one (1.429) may easily be reached.

To get the density of oxygen referred to hydrogen as unity, we must divide the answer by the weight of a liter of hydrogen (0.08987 g.). In the above case the quotient is 15.63. The accepted value is 15.89. The density referred to air as unity is similarly obtained by dividing by 1.293, the weight of a liter of air at 0° and 760 mm. pressure.

By using a modification of the flask just described, it is possible to ascertain the weights of known volumes of the vapors of liquids and solids. A temperature sufficiently high to vaporize the substance must be employed. The volume is reduced by rule to 0° and 760 mm. and the density (in this case known as the **vapor density**) is calculated as before. The reduction to 0° and 760 mm. pressure by rule gives, of course, a fictitious result. The vapor would condense to the liquid form before 0° was reached, if the cooling were actually carried out. But the value for the density *as it would be* at 0° and 760 mm. has to be calculated to facilitate comparison with the corresponding values for other substances. The results have no physical significance, but are highly important to the chemist.

Diffusion. — When two cylinders, one filled with hydrogen and one with oxygen, are placed mouth to mouth (Fig. 24), so that the one containing hydrogen Fig. 24. is uppermost, since the oxygen in the lower cylinder is nearly 16 times as heavy as the hydrogen (p. 34), we might expect the gases to remain in their respective cylinders. The oxygen, however, makes its way into the hydrogen above it, and the hydrogen penetrates into the oxygen in the lower cylinder so that, in a short time, the gases are perfectly mixed, just as if gravity did not exist. The same phenomenon is observed when,

in everyday life, a bottle of scent is opened. The vapor, on escaping, begins to penetrate in all directions through the room, showing its presence by its odor. The material of gases has in fact an independent power of locomotion. The resulting phenomenon we call *diffusion*. It is constant in rate for each gas under like conditions, and hydrogen has the greatest speed of diffusion of all the gases.

The different rates of diffusion of different gases are easily shown by comparing their several speeds with that of air, when both pass through a wall of unglazed, porous porcelain.

The porous cylinder A (Fig. 25) contains air and is connected by a rubber stopper with a wide tube which dips beneath the surface of the water. When a cylinder H containing hydrogen is brought over it, rapid escape of gas takes place through the water, showing that a rise in pressure has taken place inside the porous vessel. Before the cylinder of hydrogen approached the porous vessel, the air was moving both outwards and inwards through the porcelain, but, being the same gas, the speed of motion was equal in both directions, and therefore the pressure inside was not affected. It is important to note that there was at no time rest, there was simply equal motion in both directions. When the hydrogen atmosphere surrounded the cylinder, the hydrogen gas moved more rapidly into the cylinder than the air inside could move out, and hence an excess of pressure quickly arose in the interior.

Exact measurement shows that the lighter a gas is in bulk, the faster its parts move by diffusion in any direction. The rate is inversely proportional to the square root of the density of the gas. Thus, for hydrogen and oxygen it is in the ratio $\sqrt{1.429} : \sqrt{0.08987}$, or 4.0 to 1.
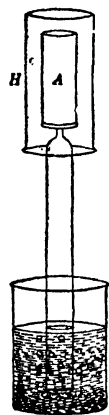
FIG. 25.

THE KINETIC-MOLECULAR HYPOTHESIS

Just as we can thoroughly understand the behavior of a watch or an automobile engine only if we know the details of its structure, and how the parts work, so we can understand the physical and chemical behavior of matter in masses only if we

are familiar with its ultimate mechanism. Hence we must now take up the study of the structure of matter in the gaseous state.

In order to *explain* the applicability of the laws of Boyle and of Charles to gases in general, a hypothesis (p. 26) has been devised by chemists. In the course of time, evidence has been accumulated which verifies this hypothesis beyond all possibility of doubt. The hypothesis is known as the 'kinetic-molecular hypothesis, from the two main postulates upon which it is based.

In the first place, it is assumed that all matter is composed of exceedingly minute particles or molecules, the molecules of any particular substance being all alike in nature and in mass. In solids and liquids, these molecules are fairly closely packed together. In gases, on the contrary, they are widely scattered, with much vacant space between them.

The second postulate is that the molecules of all substances under ordinary conditions are in rapid motion, and consequently possess **kinetic energy.** In solids and liquids this motion is restricted within a definite volume. In a gas, however, the molecules are free to distribute themselves throughout the whole of the containing vessel, and by continually striking the walls of this vessel they produce **pressure.**

The Properties of Gases. — A very noticeable fact about gases is that they *can be compressed* to an enormous extent. Oxygen at 760 mm., for example, can be reduced by pressure to one two-hundredth of its volume, or even less. The compression does not affect the individual molecules, and therefore does not diminish the volume actually occupied by the oxygen, but it crowds the molecules closer together and **diminishes** to one two-hundredth **the space** between them. Compressing a gas is, in fact, compressing the *empty space* of which it chiefly consists. To understand what follows, the reader must keep constantly before him a mental image of a jar of gas as consisting of extremely small particles separated by relatively wide, empty spaces. The molecules are in rapid motion and move in straight lines, excepting when they strike one another or the walls of the vessel.

The most remarkable property of a gas, considering the looseness with which its material is packed, is the total *absence* in it *of*

any tendency to settling or subsidence. Since the molecules cannot be at rest upon one another, as the great *compressibility* shows, we are driven to conclude that they are **widely separated from one another**, and that they occupy the space, otherwise a complete vacuum, by **constantly moving about in all directions**. But a moving aggregate of particles which does not even finally settle must be in perpetual motion. We must, therefore, believe the molecules to be wholly unlike particles of matter in having **perfect elasticity,** in consequence of which they undergo no loss of energy after a collision. They must continually strike the walls of the vessel and one another and rebound, yet without loss of motion. The fact that each gas is *homogeneous,* efforts to sift out lighter or heavier samples having failed, requires the supposition that **all the molecules** of a pure gas are **closely alike.**

The *diffusibility* of gases is due to the **motion of the molecules,** and their *permeability* to the **space** available to receive molecules of another gas. These two modes of behavior involve no additional molecular properties. The word "diffusion" is often thought to mean the property of a given mass of gas in virtue of which another gas can mix with the given mass. This property is not diffusibility but permeability. It is the other gas, which makes its way into the given gas, which is diffusing. Diffusion is spontaneous motion of the parts of a gas *away from* their original location. Unless this motion is into an empty space, the diffusing molecules must, of course, move into another body of gas. In the case of the jars of hydrogen and oxygen (p. 49), each gas moved in part *out of* its original jar (diffused), and each received parts of the other gas *into* its jar (was permeated).

From the diffusion results obtained by experiment with any particular gas, the *average speed* at which the molecules of which it is composed are moving can be calculated. For the hydrogen molecule at room temperature, this speed is 1840 meters per second, or faster than a rifle bullet. The average speed of the oxygen molecule under the same conditions is one-quarter of this value, or 460 m. per second.

Boyle's Law and Charles' Law. — Returning now to *Boyle's law* (p. 46), the thing to be accounted for is that when a sample

•of a gas diminishes in volume, its pressure increases in the same proportion. Let the diagram (Fig. 26) represent a cylinder with a movable piston, upon which weights may be placed to resist the pressure. ' Now the' pressure exercised by the gas under the piston cannot be like the pressure of the hand upon a table, since we have just assumed that the particles are not even approximately at rest, and the spaces between them are enormous compared with the size of the molecules themselves. The gaseous pressure must therefore be attributed to the colossal hailstorm which their innumerable impacts upon the piston produce. If this is the case, the compressing of a gas must consist simply• in moving the partition downwards, so that the particles as they fly about are gradually restricted to a smaller and smaller space. Their paths become on an average shorter and shorter.
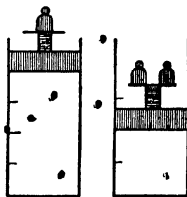
FIG. 26

Their impacts upon the walls become more and more frequent So the pressure which this causes becomes greater and greater, and is proportional to the degree of crowding (the **concentration**) of the molecules.

There are two other points to be added. When we diminish the volume to one-half, we find from experience that the pressure becomes exactly, or almost exactly, twice as great. This must mean that, although the particles are becoming crowded, they do not interfere with one another's motion, excepting of course where actual collision causes a rebound. Only in the absence of interference would doubling the number of molecules per unit of volume give exactly double the number of impacts on the walls. Hence the molecules must have practically no tendency to cohesion. Finally, the molecules must be supposed to move in straight lines between collisions.

Boyle's law therefore adds three more details concerning molecular behavior, namely, that the **crowding of the molecules** represents the *concentration of the material* and that the particles **move in straight lines** and **show almost no cohesion**, since *pressure and concentration are very closely proportional to one another.*

Dalton's law of partial pressures emphasizes the fact that these rules hold not only for single gases, but for mixtures of gases.

How, now, can we account for *Charles' law* (p. 46), according to which an increase in volume (or in pressure, if the volume is kept constant) results from heating a mass of rapidly moving molecules? The action of a particle colliding with a surface is measured in physics in terms of its mass and its velocity. It is evident that *heating* a cloud of molecules would not increase the mass of each, and it must therefore **increase the velocity of each,** since the kinetic energy of all becomes greater.

Liquefaction of Gases: Critical Temperature. — We find by experiment, finally, that all gases can be *liquefied by sufficient cooling and compression.* This fact compels us to suppose that, after all, even gaseous molecules have *some* tendency to **cohesion.** This cohesion is, in general, scarcely perceptible so long as the gas is warm and is diffuse, but it is possible, by careful measurement, to establish the fact that it does induce slight deviations from Boyle's law even under such conditions. Thus, 2 liters of oxygen at 1 atmosphere pressure, when subjected to 2 atmospheres pressure, give 0.9991 liters instead of 1 liter. The additional contraction of 0.0009 liters (0.9 c.c.) is due to the effect of cohesion when the molecules are thus crowded closer together. The gases which are more easily liquefied than is oxygen show greater effects. Thus, 2 liters of sulphur dioxide at 760 mm., when subjected to 2 atmospheres pressure, give only 0.974 liters, showing a contraction due to cohesion of 26 c.c. These data refer to 0°. At lower temperatures the contractions due to cohesion become rapidly greater.

We can readily understand, therefore, that when the kinetic energy of the molecules is sufficiently reduced by cooling, and the molecules are brought sufficiently close together, the tendency of the molecules to cohere causes the gas to condense and assume the liquid form. In 1869 Andrews found that carbon dioxide could be liquefied at 0° by 38 atmospheres pressure, and at 30° by 71 atmospheres, but that above 31.35° it could not be liquefied by any pressure. He discovered that each gas has a **critical temperature,** as he called it. For carbon dioxide, this tempera-

ture can be observed by placing a heavy-walled, glass tube (Fig. 27), half-filled with liquid carbon dioxide, in a beaker of water, and gradually raising the temperature of the latter. At 31.35°, the surface between the liquid and gas becomes hazy and vanishes. At this temperature the liquid state disappears, merging into the gaseous. When the temperature falls once more, the surface marking the boundary between liquid and gas reappears at 31.35°.

The critical temperature of oxygen is −118°, of hydrogen −234°, of carbon dioxide 31.35°, of sulphur dioxide 156°, of water 374°.

Another Deviation from the Laws of Gases.— A Perfect Gas.—It is also found by experiment that when a gas is already under very high pressure, and very closely packed, *an increase in the pressure does not produce quite as great a diminution in volume as Boyle's law leads us to expect.* This reminds us that we are **diminishing only the space between the molecules, and** not the volumes of the molecules themselves, and therefore not the total volume of the gas When, on severe compression, the volume occupied by the molecules themselves has become an appreciable fraction of the whole volume, additional compression does not affect the whole volume, and the contraction is smaller than Boyle's law would indicate. Thus, 200 liters of hydrogen, at 16° and under one atmosphere pressure, when subjected to 200 atmospheres pressure, give 1.134 liters, instead of 1 liter.

FIG. 27.

The last two effects (namely, those due to the tendency to cohesion of, and the space occupied by the molecules) are called **deviations** from the laws of gases. An imaginary gas, which exhibits neither deviation, called a **perfect gas,** is often referred to in discussing the behavior of gases.

Summary. — We may now summarize the principal facts about gases in mass, with the corresponding features of the molecular relations.

Facts About Gases in Mass.	Corresponding Relations of Molecules.
Compressibility	Vacuum + molecules widely separated.
Diffusibility	Molecules in rapid motion.
Permeability	Empty space relatively large.
Non-settling	Molecules perfectly elastic.
Homogeneity	Molecules of any one substance closely alike.
Pressure	Due to impacts of molecules.
Boyle's law	Pressure proportional to concentration of the molecules. Molecules move in straight lines and, when widely scattered, show no tendency to cohesion or to repulsion.
Charles' law	Rise in temperature increases the velocity, and therefore the kinetic energy of the molecules.
Law of diffusion . . .	Speed of molecules inversely proportional to square root of mass.
Gases can be liquefied, and show lower compressibility at high pressures	Molecules do possess *some* tendency to cohesion, and do occupy an appreciable fraction of the space when pressure is very great.

History of the Kinetic-Molecular Theory. — This theory was first suggested by Daniel Bernoulli (1738), who explained by its means the pressure and compressibility of gases. Lomonossov (1748) developed the theory very completely and by means of it explained Boyle's law and the effects of changes in temperature. He also anticipated from the theory the existence of the second deviation from the law of gases (1749), a discovery usually credited to Dupré (1864). He likewise pointed out that there was no limit to the maximum velocity of a molecule, and therefore no upper limit of temperature, but that there must be a lower limit (the absolute zero) at which the molecules would be at rest (1744). This work was entirely forgotten, until attention was called to it in 1904 by Menschutkin.

Similar views were expressed by Waterston (1845), but were still so much ahead of the time that the committee of the Royal Society did not approve the paper for publication, and it was discovered in the archives of the society, long afterwards, by Lord Rayleigh. The development of the theory, so far as it applies to heat, is therefore credited to Joule (1855-60) and, in respect to all properties of gases, to Krönig (1856) and Clausius (1857), who knew nothing of the earlier work.

Exercises. — The text cannot be understood unless some problems involving the laws of gases are actually worked.

1. Reduce 189 c.c. of gas at 15° and 750 mm. to 0° and 760 mm.

2. Reduce 110 c.c. of gas at -5° and 741 mm. to 0° and 760 mm.

3. Convert 500 c.c. of gas at 25° and 700 mm. to 18° and 745 mm.

4. Reduce 250 c.c. of gas (standing over water) at 22° and· 755 mm. to the dry condition and to 0° and 760 mm.

5. The density of a substance referred to air is 3.2. What is the density referred to hydrogen? What will be the volume occupied by 10 g. of the substance at 20° and 752 mm.?

6. What will be the relative rate of diffusion of the substance in question 5, (a) to hydrogen, (b) to air?

CHAPTER V

HYDROGEN

HAVING learned something of the properties of gases in general, and of oxygen in particular, we turn now to water, a substance as closely connected with our daily life as is air. We have seen (p. 36) that it is a compound of oxygen and hydrogen, and the latter element, therefore, may be taken up next. Hydrogen is of interest on its own account because it is often used in filling balloons, and nearly half the bulk of ordinary illuminating gas is free hydrogen.

History. — That hydrogen is a distinct kind of gas was first established by Cavendish (1766). Somewhat later (1781), he showed that, when it burned in the air, it gave a vapor which could be condensed to liquid water. Since oxygen was then known to be the substance with which combustibles united, this proved that water was a compound of hydrogen (Greek, *water producer*) and oxygen.

Occurrence. — Free hydrogen is found, mixed with varying proportions of other gases, in exhalations from volcanoes, in pockets found in certain layers of the rock-salt deposits, and in some meteorites. The air contains not over 1 part in 1,500,000. The lines of hydrogen are prominent in the spectra of the sun and of most stars.

In combination, it constitutes about 11 per cent by weight of water. It is an essential constituent of *all* acids. It is contained also, in combination with carbon, in the components of natural gas, petroleum, and all animal and vegetable bodies.

Preparation by the Action of Metals on Cold Water. — To liberate hydrogen from water, it is necessary to use some ele-

\ment with which the oxygen of the water will combine even more eagerly than with hydrogen, and to offer this element in exchange for the hydrogen.

The more active metals, such as potassium, sodium, or calcium, displace hydrogen rapidly from cold water. Potassium and sodium are lighter than water and float on the surface. In the case of the former, so much heat is liberated that the hydrogen catches fire, and with neither metal is the experiment safe in the hands of a novice. Calcium sinks to the bottom, and acts rapidly, but not violently, so that the gas is easily collected (Fig. 28). The pieces of these metals, of course, act upon only a small part of the water in the vessel. In each case the metal displaces one-half only of the hydrogen in that part of the water upon which it acts. The other products are the hydroxides of potassium, sodium, and calcium, respectively. The two former dissolve in the excess water, leaving a clear liquid when the metal is all gone, but may be recovered as white solids by evapora-

FIG. 28.

tion. The calcium hydroxide (slaked lime) is dissolved only in part, and much of it may be seen suspended in the water after the action.
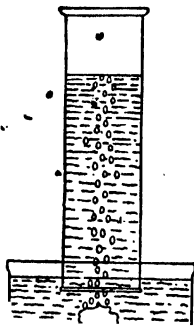
Potassium (78.2) + Water (36.032) →
          Potassium hydroxide (112.216) + Hydrogen (2.016)
Calcium (40.07) + Water (36.032) →
          Calcium hydroxide (74.086) + Hydrogen (2.016)

An alloy of lead with sodium (35 per cent), sold under the name of **hydrone**, affords a convenient substitute for sodium in the foregoing actions.

Displacement. — These actions, in which hydrogen is liberated, present us with a new — the third — variety of chemical change. Here **an element displaces one of the elements from a compound**, setting it free, and **unites with the rest of the constituents of the compound.** Thus, calcium displaces part of the

hydrogen, and unites with the oxygen and · the rest of the hydrogen.
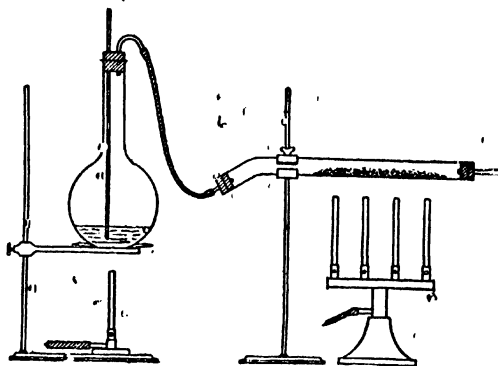
FIG. 29.

Hydrogen from Metals and Water at a High Temperature.—
With **steam** at a red heat, metals like iron, zinc, and magnesium
interact vigorously. The steam, generated in a flask, enters at
one end of the tube containing the metal (Fig. 29), and the
hydrogen passes off at the other. Since, at a red heat, all hy-
droxides, except those of potassium and sodium, are decomposed
into an oxide of the metal and water, the *oxides* are formed in
this case:

Magnesium (24.32) + Water (18.016) →
        Magnesium oxide (40.32) + Hydrogen (2.016)
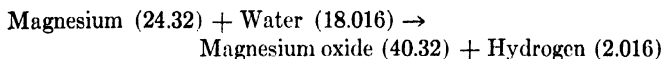
Iron, under the above conditions, gives the magnetic oxide (com-
pare p. 36):

Iron (167.52) + Water (72.064) →
        Magnetic oxide of iron (231.52) + Hydrogen (8.064)
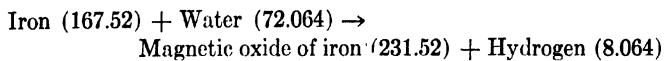
Silver, gold and platinum, which do not combine directly with
pure oxygen, and even copper and mercury, which do, are all
unable to form oxides and to liberate hydrogen when heated in
steam.

Acids. — In making hydrogen in the laboratory, dilute acids are used almost exclusively. The most common acids are **hydrochloric acid** and **sulphuric acid**. The former is a solution of a gas, hydrogen chloride, in water. The "pure concentrated" hydrochloric acid used in laboratories contains nearly as much of the gas (39 per cent by weight) as the water will dissolve. The "commercial" acid contains impurities and is also less concentrated. The "concentrated" sulphuric acid is an oily liquid containing practically no water. The pure acid is a compound of hydrogen, sulphur and oxygen, to which chemists have given the name *hydrogen sulphate*. The "commercial" sulphuric acid contains 6 to 7 per cent of water, besides impurities.

All the "dilute" acids contain 70 to 80 per cent of water. The water, as a rule, takes no part in the chemical changes in which the acids are concerned, and is therefore omitted from the condensed statements of their reactions.

The name "acid" is restricted to one class of substances having certain definite characteristics, which will be discussed in detail in a later chapter. It will suffice to mention at this point that *hydrogen* is the one essential constituent of all acids, that their aqueous solutions have a sour taste and change the color of litmus from blue to red, and that, in aqueous solution, also, their hydrogen is displaced, in whole or in part, by certain metals.

Radicals. — In describing the chemical behavior of acids, we speak of the hydrogen as the **positive radical,** because in electrolysis (see p. 65) it is attracted to the negative pole, and of the material combined with the hydrogen as the **negative radical,** because it is attracted to the positive pole. Thus in hydrochloric acid hydrogen is combined with the chloride radical, in sulphuric acid with the sulphate radical. The first is a simple radical, containing only chlorine, the second is a compound radical, containing sulphur and oxygen. In many interactions the compound radicals move as units from one state of combination to another.

Preparation of Hydrogen by Displacement from Diluted Acids, — Every one of the metals which displace hydrogen from

water will also displace it from dilute acids. The acids *must be* *diluted with water*, unless, like hydrochloric acid, they are already dissolved in water. The action is much more vigorous than that on water, so that the most active metals are not employed. Metals like zinc, iron, and aluminium serve the purpose. The metal combines with the negative radical, and so liberates the hydrogen, which escapes in bubbles. When excess of the metal is employed, hydrogen continues to be evolved until the acid present is all used up, and evaporation of the clear liquid which remains will then give in dry form the compound of the metal with the negative radical. Thus, with zinc and dilute sulphuric acid, zinc sulphate is produced.

Zinc (65.37) + Sulphuric acid (98.076) →
                    Zinc sulphate (161.43) + Hydrogen (2.016)
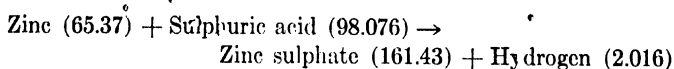
With aluminium and hydrochloric acid, the product is aluminium chloride:

Aluminium (54.0) + Hydrochloric acid (218.808) →
                    Aluminium chloride (266.76) + Hydrogen (6.048).
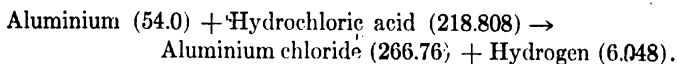
The water undergoes no change during the action, although its presence is essential. It is simply a part of the apparatus. Any acid may be used, although with many the action goes on very slowly.
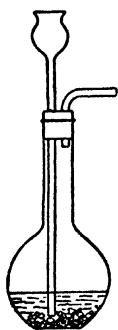
For preparing small amounts of hydrogen, the apparatus (Fig. 30) is such that additional acid may be added through the thistle-, or safety-tube, as desired. This avoids opening the flask and admitting air. The gas may be caught like oxygen over water or, being lighter than air, may be collected by **downward displacement** of the latter (Fig. 31a). Heavy gases are collected by **upward displacement** of air (Fig. 31b).

With a Kipp's apparatus (Fig. 32) the gas may be made on a large scale and its delivery can be regulated. When the stream of gas is shut off by the stopcock, the pressure of the gas, as it continues to be generated, drives the acid away from the metal and up into the globe above,

Fig. 30.

so that the action ceases. Yet the action is ready to begin again the moment any portion of the stored gas is drawn off for use.
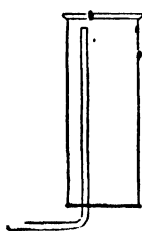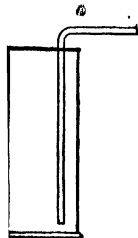
FIG. 31a.   FIG. 31b.

Contact of the zinc or iron with an inactive metal, like platinum or copper, forms an electrical couple and hastens the inter-action. For the same reason, commercial zinc, which contains traces of other metals, gives a steady evolution of hydrogen, while extremely pure zinc is almost inactive.

The Proportions by Weight.—It may be well to remind ourselves that the weights of the various materials (given in brackets) are obtained by laboratory measurements. It is always found that the total weight of the product is exactly equal to that of the materials used (p. 24). Also, that a given weight of the metal, say zinc, will always displace and liberate the same weight of hydrogen. Also, that the proportions by weight of the constituent elements in the compound produced are always the same (p. 23). If we place a weighed piece of zinc in hydrochloric acid, and wait until the zinc has all disappeared, we can then boil away the water and unused acid, and weigh the white, solid zinc chloride. We find that 65.37 grams of zinc always leave 136.29 grams of zinc chloride. The difference, 70.92, is the chlorine, and whatever weights we take, the proportion of zinc to chlorine in the zinc chloride is always in the ratio 65.37 : 70.92.

FIG. 32.

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Zinc (65.37) + Hydrochloric acid → Hydrogen (2.016) + Zinc chloride
        (72.936)   (136.29)
    Hydrogen 2.016   Zinc 65.37
    Chlorine 70.92   Chlorine 70.92

Chemically Equivalent Quantities. — It will be observed that
65.37 parts of zinc displace 2.016 parts of hydrogen, whether the
acid used is sulphuric acid or hydrochloric acid. The proportion
is, in fact, the same with every acid. Hence 65.37 parts of zinc
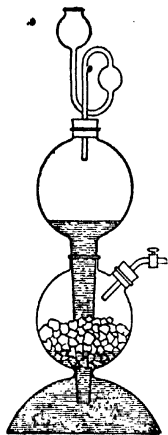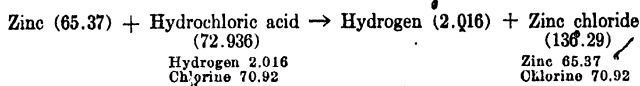and 2.016 parts of hydrogen are spoken of as **chemically equivalent**
quantities. The quantities of the displacing and of the displaced
element are in all cases referred to as chemically equivalent.

The term equivalents is applied also to the quantities *liberated
by decomposition* of a compound like the 200.6 parts of mercury
and the 16 parts of oxygen (p. 23). It is likewise used of the
proportions *combining* when chemical union takes place, as in
the case of phosphorus 124.16 parts and oxygen
160 parts (p. 36). The proportions of the elements
in zinc chloride (see above) are also chemically
equivalent.

Chemically equivalent quantities (or, simply, **equiv-
alents**) of two substances are exact **quantities which
enter into or result from a chemical reaction.**

ORDER OF
ACTIVITY.
Metals
Potassium
Sodium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Copper
Mercury
Silver
Platinum
Gold

The Order of Activity of the Metals. — It will
greatly aid us in remembering a number of the facts
already given, as well as many others, if we compare
carefully with those facts the order in which the
metals stand in the adjoining list. The most active
metals are at the top. All above hydrogen displace
this element from dilute acids (and, with more diffi-
culty, from water); those below it do not.

The first displaces the hydrogen from water so
violently that the gas catches fire, the second dis-
places it vigorously, the third less vigorously. Mag-
nesium requires hot water and iron superheated
steam. Copper and the metals following it do not liberate hydro-
gen from water.

Again, the upper metals act too violently on dilute acids, and

zinc is used to prepare the gas. Copper and the metals following it do not displace hydrogen from dilute acids.

Still again, we recall the fact (p. 36) that, when we heat metals in pure oxygen, the last three do not become oxidized at all. Those preceding silver do combine with pure oxygen — mercury with difficulty, and the others more and more vigorously as we ascend the list. On the other hand, if we start with the oxides of all the metals, we find that those at the foot of the list, up to and including mercuric oxide lose all their oxygen when heated, leaving the metal.

Other facts of a similar nature will be mentioned as we encounter them. Meantime, it may be noted that the metals found uncombined in nature are those following hydrogen. Again, the metals known to have been first used by the human race were gold and silver. In the "bronze age" means of liberating copper from its ores had been discovered. Lead, tin, and iron came later. The list, read from the bottom up, gives, therefore, roughly, the historical order in which the metals came into use.

Preparation of Hydrogen by Electrolysis. — If we dissolve *any acid* in water, and immerse the wires from a battery in the solution, bubbles of hydrogen begin to appear on the *negative* plate (the cathode) and rise to the surface. All the other constituents, whatever they may be, are attracted to the positive plate (the anode) and, therefore, do not interfere with the collection of pure

FIG. 33.

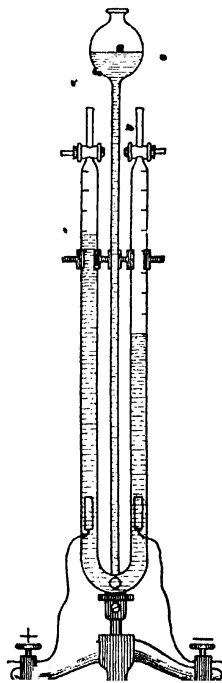hydrogen. An apparatus devised by Hofmann (Fig. 33) enables us to secure the hydrogen, which ascends on the right and accu-

mulates at the top of the tube, displacing the solution. What
may be liberated at the positive plate depends upon the acid
used. With hydrochloric acid, it is chlorine; with sulphuric acid,
oxygen comes off and sulphuric acid is regenerated.

Hydrochloric acid   →   Hydrogen   +   Chlorine
(in aqueous solution)   (at negative plate)   (at positive plate)

Decomposition of a compound by the use of electric energy is
called **electrolysis** (Greek, *decomposition by electricity*). •

Other Ways of Preparing Hydrogen. — For special pur-
poses, hydrogen may be made by boiling an aqueous solution
of sodium hydroxide with aluminium turnings, when sodium
aluminate is formed; also by heating powdered zinc and dry
sodium hydroxide, the product being sodium zincate. These reac-
tions will be discussed later, under aluminium and zinc
respectively.

Sources of the Hydrogen of Commerce. — Zinc is too expen-
sive a substance to use in the preparation of hydrogen in large
quantities for commercial purposes. We realize this when we
note that 65 parts of zinc will liberate only 2 parts of hydro-
gen from hydrochloric or sulphuric acid, so that with 1 ℔. of
zinc we obtain only one half-ounce of the gas. Different sources
are used in different localities and countries.

A limited quantity is obtained as a by-product in the electrol-
ysis of an aqueous solution of common salt (sodium chloride),
in connection with the manufacture of caustic soda (sodium
hydroxide, p. 170). The hydrogen is collected and compressed
in steel cylinders.

In some circumstances, the method of passing steam over
heated iron is used (p. 60).

The largest amount of commercial hydrogen, however, is made
by purification of water-gas, which is a mixture of hydrogen
and carbon monoxide (p. 426). This, and still other processes,
involve substances and reactions which we have not yet en-
countered, and will be mentioned at the appropriate points.

Physical Properties. — Hydrogen is a colorless, tasteless,
odorless gas. One liter weighs only 0.08987 g., while one liter of

air weighs 1.293 g. Air is thus 14.5 times heavier, and hydrogen can be poured upwards (Fig. 34) and is used for filling balloons. Hydrogen was first liquefied in visible amounts by Dewar (1898). The critical temperature is – 234°. The colorless liquid boils at – 252.5°, and, when allowed to evaporate rapidly under reduced pressure, freezes to a colorless solid (m.-p. – 260°). All other gases, except helium, solidify easily when led into a vessel surrounded by liquid hydrogen.
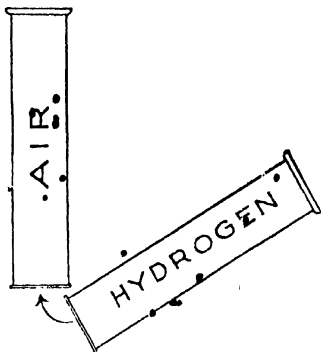
Fig. 34.

Hydrogen is even less soluble in water than is oxygen, 1.8 volumes of the gas dissolving in 100 volumes of water at 20°. Hydrogen is adsorbed, for the most part in a purely mechanical way (see p. 139), by many metals. The maximum adsorbed by palladium under favorable conditions is 873 volumes.

Chemical Properties. — Hydrogen, delivered from a jet, burns in air or pure oxygen. A cold vessel held over the almost invisible blue flame condenses to droplets of water the steam that is produced (Fig. 35). When hydrogen and oxygen are mingled in a suitable burner (Fig. 36), although the flame gives little light,
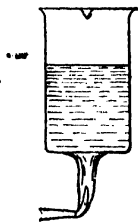
Fig. 36.

Fig. 35.
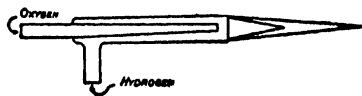
it is exceedingly hot. Platinum melts in it easily and an iron wire burns brilliantly. In a closed space it produces a tempera-

ture of over 2500°. When the flame is allowed to play on a piece of quicklime, the latter becomes white-hot at the spot where the flame meets it." This result is called a **calcium light** or **lime light**.

When hydrogen and oxygen are mixed, the chemical action is very slow at ordinary temperatures, *no perceptible amount of union occurring in a period of five years*. If the mixture is sealed up and kept at 300°, after several days a small part is found to have combined to form water. At 518°, hours are required before the union is complete. At 700° the combination is almost instantaneous. Hence contact with a body at a bright-red heat is required actually to explode the mixture.

Finely divided platinum, when held in the cold mixture, hastens the union (otherwise vanishingly slow) in the part of the gases in contact with it. The heat of the union raises the temperature of the platinum and of neighboring portions of the gas and causes explosion of the mass. The platinum is simply a contact agent (p. 33) and remains itself unaffected.

Hydrogen unites directly with a minority only of the simple substances. It combines rapidly with oxygen, chlorine, fluorine, and lithium, and more slowly with a few others.

Hydrogen acts also upon some of the compounds of metals with oxygen or chlorine. Thus, when an oxide of iron or of copper is heated in a tube in a stream of hydrogen, water is produced and the metal remains:

Magnetic oxide of iron (231.52) + Hydrogen (8.064) →
          Iron (167.52) + Water (72.064)
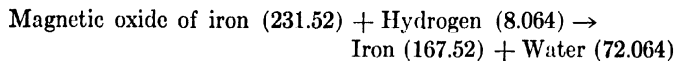
Oxides of metals above iron in the "order of activity" (p. 64), however, are very stable. Hydrogen is unable to remove the oxygen from such oxides and leave the metal.

Reduction. — The removal of oxygen from a compound by its union with some other substance is called **reduction** and the substance, (in the foregoing instance, hydrogen) is called a **reducing agent.** Carbon, in the form of coal or coke, is the agent of this kind most commonly used in chemical industries. The term

reduction is applied to some other chemical actions, in which oxygen is not concerned. In all cases, however, reduction is the opposite of oxidation (p. 41).

Exercises. — 1. Name three varieties of chemical change (pp. 11, 19, 59) and explain the difference between them.

2. What do you infer as to the composition of a substance when it is named: (*a*) an oxide, (*b*) an hydroxide (p. 60)?

3. What weight of hydrogen would be obtained by the action of excess water on (*a*) 100 g. potassium, (*b*) 100 g. calcium? What weight would be obtained by the action of excess steam on (*a*) 100 g. magnesium, (*b*) 100 g. iron?

4. To which of the three varieties of chemical change does the action of hydrogen on magnetic oxide of iron (p. 68) belong?

THIS is the most important, as well as the most plentiful, of all compound substances. The human body is saturated with it, and water to make up for evaporation, as well as to aid in digestion, is a most necessary part of our food. The ocean covers about three-fourths of the surface of the earth, and the "dry" land would be uninhabitable if it were really dry. The air always contains more or less water vapor.

Measurement of the Composition by Weight. — An arrangement by which the proportion by weight of hydrogen and oxygen
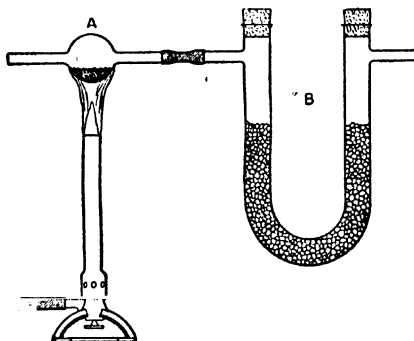
FIG. 37.

in water can be determined is shown in Fig. 37. The bulb **A** contains cupric oxide, which is heated. Hydrogen from a generator or cylinder enters on the left and reduces the oxide, forming copper and water:

Hydrogen + Cupric oxide → Water + Copper.
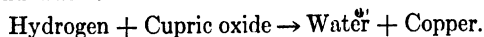
The water is carried as vapor by the excess of hydrogen and passes into the U-tube **B**. This tube contains calcium chloride, a substance which absorbs water greedily and is used therefore

70

for drying gases. Here the water is all caught, while the hydrogen passes on. The tubes A and B with their contents are weighed just before, and again just after, the experiment. The loss of weight in A is the weight of the oxygen. The gain in weight in B is the water. The difference between these numbers is the hydrogen. It is found that the weights of hydrogen and oxygen thus ascertained always stand in a ratio close to 1 (Hydrogen) : 7.94 (Oxygen) or 1.008 : 8, the proportions accurately determined by Morley.

Measurement of the Composition by Volume. — The proportions by volume in which hydrogen and oxygen combine may be shown by introducing the two gases into a tube, filled with mercury and inverted in a cylinder of mercury (Fig. 38). The volumes, at atmospheric pressure, are read by lowering the tube, after the introduction of each gas, until the levels of the mercury inside and outside are alike. A spark from an induction coil passed between the platinum wires inserted at the top of the tube causes the union of the gases. The water condenses to a slight dew and the volume of the single gas which remains is measured. Thus, if 19.5 c.c. of oxygen and 20 c.c. of hydrogen are taken, the volume of gas remaining is 9.5 c.c. and this gas is afterwards found to be oxygen (test, p. 37). The volumes consumed were therefore 19.5 – 9.5 = 10 c.c. of oxygen and

FIG. 38.

20 c.c. of hydrogen. The ratio by volume is therefore 2 Hydrogen: 1 Oxygen. If these exact proportions are used, the mercury fills the tube after the explosion, but is apt to break it by striking the top violently.
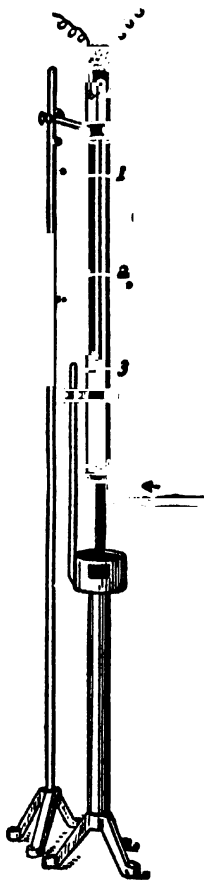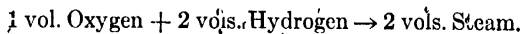
By taking the gases in the exact ratio 1 : 2, and surrounding the tube by a wider one through which steam passes, the condensation of the resulting steam is prevented. It is found that, 'when all the gases are measured at the same temperature (here about 100°), a shrinkage of one-third occurs. That is to say:

1 vol. Oxygen + 2 vols. Hydrogen → 2 vols. Steam.

Gay-Lussac's Law of Combining Volumes. — When other chemical actions between gases are studied in the same way, it is found that, in every case, **the volumes of the gases used and produced in a chemical change can always be represented by the ratio of small whole numbers.** This fact is exceedingly interesting. It was first discovered by Gay-Lussac in 1808. There is no such simple relation amongst the proportions by *weight*, which usually can be expressed only by large numbers (see p. 36) or by irregular fractions, so that this evidence of the existence of a simple rule in regard to combining proportions is the first we have encountered and is very welcome. The use made of it by the chemist will be developed in the next chapter.

Physical Properties of Water. — A deep layer of water has a blue or greenish-blue color. At a pressure of 760 mm., water exists as a liquid between 0° and 100°. Below 0° it becomes solid, above 100° a gas. Of all chemical substances it is the one which we use most, so that its physical properties, discussed below, should be studied attentively. Then, too, what is said of water is in general true of all other liquids, from which it differs only in details.

The average quantity of heat required to raise one gram of water one degree in temperature, between 0° and 100°, is called a **calorie**, the unit quantity of heat. The specific heat of any substance being the quantity of heat required to raise the temperature of one gram of the substance one degree, the average specific heat of water throughout this temperature range is 1. The values at 0° and 100° are slightly higher than those in the middle of the range, but the variation from unity is never so great as 1 per cent. The values for all other common materials are much smaller (*e.g.*, limestone 0.2). Thus the temperature of large

masses of water, such· as lakes and seas, changes more slowly, and within a smaller range, than that of the rocks and soil composing the land. The more, constant temperature of the water tends to regulate that of the air, and hence the climate of an island. is less variable from season to season than is that of a continent.

The weight of a cubic·centimeter of water at 4° is.1 gram. At this temperature water possesses its *maximum density;* not only· does it expand when heated, but it also·expands slightly when cooled. Thus a kilogram of water at 0° occupies 1000.13 c.c., or 0.13 c.c. more than at 4°. The volume of a kilogram of water at 100° is 1043.2 c.c. Nearly every substance contracts regularly on cooling, and this expansion of water between 4° and 0° is very unusual.

Perfectly pure water is an *exceedingly* poor conductor of electricity. Ordinary tap-water owes its small capacity for conducting almost entirely to traces of impurities (see p. 80). Many substances, however, when dissolved in water, give solutions which are extremely good conductors. Sulphuric and hydrochloric acids are examples which we have already encountered (p. 65). This is a point which will be·taken up in detail later.

Ice. — The raising or lowering of the temperature of a gram of water through one degree involves, we have seen above, the addition or removal of approximately one calorie of heat. The conversion, however, of a gram of water at 0° to a gram of ice at 0° requires the removal of 79 calories. The mere melting of a gram of ice causes an absorption of heat to the same amount, called the **heat of fusion of ice.** At 0° a mixture of ice and water will remain in unchanged proportions indefinitely. Any cause which tends *permanently* to lower or raise the temperature by a fraction of a degree, however, will bring about the disappearance of the water or of the ice, respectively. This *equilibrium* temperature is called the **melting-** or the **freezing-point.**

Water can be cooled below 0° (supercooled) without beginning to freeze, unless it is stirred, or "inoculated" by the addition of a piece of ice. Hence, the freezing-point is not defined as the point at which ice begins to form, for that point varies, and is always below 0°, but as the temperature of a *mixture* of ice and water.

Water expands very considerably on solidification, a kilogram of ice at 0° occupying 1090.83 c.c., or 90.7 c c. more than an equal weight of water at the same temperature. This is again very unusual, since nearly all substances contract on changing from the liquid to the solid state. It plays a very important part, however, in the economy of nature. If ice were heavier than water, it would sink to the bottom as soon as formed, and rivers and lakes would soon become entirely frozen.

Steam. — At atmospheric pressure, water passes into steam ("boils") rapidly at 100°, but at lower temperatures, and even when frozen, it does the same thing more slowly. It changes into steam, however, only when the necessary supply of heat is forthcoming. One gram of water at 100°, in turning into a gram of steam at 100°, takes up 540 calories. This is called its **heat of vaporization.** Steam, in fact, contains much more internal energy than an equal weight of water at the same temperature, just as water, in turn, contains more energy than ice. At 100° steam occupies nearly 1600 times the volume of an equal weight of water.

Steam is a colorless, invisible gas. The visible cloud of fog, seen when steam escapes into cold air, is composed of minute drops of water, formed by condensation, and visible because they have *surfaces* and reflect light.

The States of Matter: Transition Points. — Most substances are known in three different states of aggregation, a solid (or crystalline), a liquid, and a gaseous form. There is no magic about the number, three, however. Thus, sulphur has a vapor state, two liquid states, and several different crystalline forms. There are no fewer than five forms of ice, different in *physical* but identical in *chemical* properties.

All transitions from one state to another take place at some definite temperature (when the pressure is fixed). Such temperatures, when referring to the change from the solid to the liquid, and from the liquid to the gaseous state, are called the melting-point or freezing-point, and the boiling-point, respectively, or in general, are known as **transition points.**

When we wish to transform a substance from one state to another, we change its *conditions* (see p. 11). Thus under atmospheric pressure water is converted to ice by reducing the temperature below 0°, and to steam by raising it above 100°. Under a pressure of 100 atmospheres, however, water freezes at – 1°, and boils only at 630°. With still higher pressures, the change in the freezing-point is much more marked. Thus under 2000 atmospheres pressure water does not freeze above – 20°. If the pressure is increased further, different crystalline forms of ice make their appearance, and the freezing-point rises again until under 20,000 atmospheres water is found to freeze at + 78° !

Aqueous Tension and Vapor Pressure. — The transition of water from the liquid to the gaseous state deserves somewhat more extended study.

The most significant fact about this transition is that, *when excess of the liquid is present,* the pressure of the vapor above the liquid quickly reaches a definite maximum value for each temperature. In the absence of excess of the water, *less* than this maximum pressure may exist. *More* than the maximum pressure proper to a given temperature, if produced by compression, cannot be maintained, however, for a part of the vapor condenses to the liquid state. The magnitude of this maximum vapor pressure, at a given temperature, depends on the tendency of the particular liquid to pass over into vapor. This maximum vapor pressure is held, therefore, to represent the **vapor tension of the liquid,** at the given temperature, and this is a specific property of the substance.

The vapor tension may be shown by allowing a few drops of water to ascend into a barometric vacuum (Fig. 39). The tube on the left shows the original height of the mercury in the barometer. The tube on the right shows the result of admitting the water. The difference in the
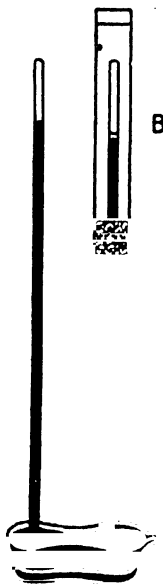

FIG. 39.

height of the two columns gives the value of the vapor pressure of the water vapor. With excess of water, the value is that of the vapor tension, called, in the case of water, the **aqueous tension.**

The jacket surrounding the tube on the right enables us, by adding ice or warm water, to maintain any temperature between 0° and 100°. When ice is used outside, and a piece of it is introduced into the vacuum, the vapor it gives off quickly reaches a pressure of 4.6 mm. The vapor pressure of the ice takes the place of 4.5 mm. of mercury in balancing the atmospheric pressure, and so the mercury column falls by this amount. Similarly, water at 10° causes a fall of 9.1 mm. and at 20° of 17.4 mm., so that these represent the mercury-height values of the aqueous tension at these temperatures. The *quantity* of water used makes no difference, so long as *a little more* is present than is required to fill the available space with vapor. With ether, instead of water, at 10°, the fall is 28.7 mm.

With water at higher temperatures the fall of the mercury column becomes much greater. At 50° it is 92 mm., at 70° it is 233.3 mm., at 90° it is 525.5 mm., and at 100° it is 760 mm., or one atmosphere. At 121° the aqueous tension is two atmospheres, at 180° it is ten atmospheres (see Appendix III).

When water at a certain temperature has given the full amount of water vapor to the space above it that its aqueous tension permits, we say that the space is **saturated** with vapor. That **concentration** of vapor which constitutes saturation varies with the temperature of the water and depends, therefore, solely on the power of the water to give off vapor. It has nothing to do with the size of the space, and is even independent of other gases the space may already contain. Thus, if a little air is first placed above the dry mercury (Fig. 39), causing it to fall, the *additional* depression produced by adding water is the same as if the air had been absent (Dalton's law of partial pressures, p. 47).

The Properties of Liquids and the Kinetic-Molecular Hypothesis. — The fact that even great pressures produce little diminution in the volume of a liquid shows that the free space,

so predominant in gases, is relatively unimportant in liquids. This is only natural in view of the smaller volume occupied by substances in the liquid state. Thus we have seen (p. 74) that steam at 100° occupies nearly 1600 times the volume of an, equal weight of water. To reduce the volume of water to four-fifths requires, not raising the pressure to five-fourths as in the case of steam, but increasing it from 1 to 10,000 atmospheres. Evidently the molecules are already very closely packed.

This close packing of the molecules causes *cohesion* to be much more pronounced in liquids than in gases. A small amount of liquid, when poured into a vessel, does not fill the whole of the available space, but forms coherent drops, the curvature of the surface of which indicates that tremendous forces are exist-ent, pulling the outside molecules towards the interior of the liquid. Nevertheless, molecules do escape outwards from a liquid surface to form vapor (see pp. 75-76). We must therefore con-clude that the molecules of a liquid are still in rapid motion. Similarly, when liquids which are capable of mixing (*e.g.*, alcohol and water) are placed in separate layers in the same vessel, they do mix, slowly, by *diffusion*. The rate of dispersion of the mole-cules, although much impeded by their close packing, has not been annihilated.

A liquid still possesses, therefore, in a modified degree, many of the properties exhibited by a gas. For any particular sub-stance, the differences between the behavior of the liquid and the gaseous states grow less and less as the temperature is raised, until at the *critical temperature* (see p. 54) the two states become identical.

Molecular Relations of Liquid and Vapor. — When the water was introduced above the barometric column, the vapor, or gaseous water, could have resulted only from the spontaneous motion of the molecules in the liquid. Some of the molecules, moving near the surface, went off into the space above the water and became gaseous. To be consistent, we must also conclude that the vapor above the water is not composed of the *same* set of molecules one minute as it was during the preceding minute. Their motions must cause many of them to plunge into the

liquid, while others emerge and take their places. When the water is first introduced, there are no molecules of vapor in the space at all, so that emission from the water predominates. The pressure of the vapor increases as the concentration of the molecules of vapor becomes greater, hence the mercury·column falls steadily. At the same time the number of gaseous molecules plunging into the water per second must increase in proportion to the degree to which they are crowded in the vapor. The rate at which molecules return to the water thus begins at zero, and increases steadily; the rate at which molecules leave the water maintains a constant value. Hence the rate at which vapor molecules enter the water must eventually equal that at which other water molecules leave the liquid. At this point, occasion for visible changes ceases and the mercury comes to rest. We are bound to think, however, of the exchange as still going on, since nothing has occurred to stop it. The condition is not one of rest but of rapid and equal exchange. Such, described in terms of molecules, is the state of affairs which is characteristic of a condition of **equilibrium.** The condition is dynamic, and not static.

Equilibrium. — This term is used so often in chemistry, and is used in so unfamiliar a sense, that the reader should consider attentively what it implies. Three things are characteristic of a state of equilibrium:

1. There are **always two opposing tendencies** which, when equilibrium is reached, balance each other. In the foregoing instance, one of these is the hail of molecules leaving the liquid, which is constant throughout the experiment. It represents the **vapor tension of the liquid.** The other is the hail of returning molecules, which, at first, increases steadily as the concentration of the vapor becomes greater. This is the **vapor pressure of the vapor.** These have the effect of opposing pressures and, when the latter becomes equal to the former, *equilibrium* is established. In all the cases of equilibrium which will be encountered, we shall symbolize the two opposing tendencies by *two* arrows, thus:

Water . (liquid) ⇌ Water (vapor).

2. Although their effects thus neutralize each other at equilib-
rium, both tendencies are still in full operation. In the case in
point, the opposing hails of molecules are still at work, but
neither can effect any visible change in the system. Equilibrium
is a state, not of rest, but of balanced activities.

3. (This is the *chief* mark of equilibrium.) A slight change
in the conditions produces, never a great or sharp change, but
always, and instantly, a corresponding small change in the state
of the system. The change in the conditions accomplishes this
by favoring or disfavoring one of the two opposing tendencies.
Thus, for example, when the *temperature* of a liquid *is raised,* the
motion of its molecules is increased, the rate at which they leave
its surface becomes greater, the vapor tension increases and,
hence, a greater concentration of vapor can be maintained. The
system, therefore, quickly reaches a new state of equilibrium in
which a higher vapor pressure exists.

In the preceding illustration, the evaporating tendency was
favored by a rise in temperature. As an example of a change in
conditions *disfavoring* one tendency, take the case where the
liquid is placed in an *open,* shallow vessel. Here the condensing
tendency is markedly discouraged, for there is little chance of
return of the emitted molecules. Hence complete evaporation
finally takes place. Elevation of the temperature hastens the
process. A draft insures the diffusion of the vapor away from
the surface of the liquid, and has therefore the same effect. The
two methods of assisting the displacement of an equilibrium,
and particularly the second, in which the opposed process is
weakened and the forward process triumphs solely on this
account, should be noted carefully. They are applied with sur-
prising effectiveness in the explanation of chemical phenomena
(see Chaps. XV and XVIII).

Water as a Solvent. — The physical property of water most
frequently made use of in chemical work is its remarkable power
of *dissolving* many other substances. This subject is so im-

portant and extensive that we shall presently devote a complete chapter to some of its simpler and more familiar aspects.

Natural Waters. — The foreign material in natural waters is divided into **dissolved** matter and **suspended** matter. Rain-water, collected after most of the dust has been carried down, is the *purest* natural water. It contains, however, nitrogen, oxygen, and carbon dioxide dissolved from the air. Sea-water holds about 3.6 per cent of dissolved material. River and, especially, well waters dissolve various substances during their progress over or under the surface of the ground. They often contain calcium sulphate, calcium bicarbonate, and compounds of magnesium, which act chemically upon soap (p. 502), and are then described as **hard.** Sometimes they contain compounds of iron, and sometimes they are effervescent and give off carbon dioxide. These are called mineral waters.

Many river waters contain large amounts of clay and organic matter (often due to admixture of sewage) suspended in them. It is not the organic matter which is deleterious, but the bacteria of putrefaction and disease which are present also, and are usually for the most part attached to the particles of suspended matter. Cholera and typhoid fever are often spread by the drinking of water into which sewage, infected by other patients suffering from these diseases, has been allowed to enter. Clay can be seen, and renders the water turbid, but organic matter and bacteria may be present in water which looks perfectly clear.

Purification from Suspended Matter. — The suspended impurities, including the bacteria, may be removed by **filtration.** On a large scale, beds of gravel are employed, but this treatment will not remove all bacteria. In many cases small amounts of alum, or alum and lime, or ferrous sulphate (copperas) and lime, are added. These produce slimy precipitates, which assist in the elimination of fine, suspended inorganic and organic matter. This is called the **coagulation treatment** (p. 585). The whole suspended matter is then allowed to settle, which it does very quickly, in large reservoirs. Any remaining organisms may be

destroyed by adding a little bleaching powder (p. 296), before the water is distributed.

In the household, the **Pasteur filter** is the most compact and efficient appliance. The water enters at the top (Fig. 40), and is forced inwards by its own pressure through the pores of a cylinder of unglazed porcelain. The cylinder must be taken out, and its exterior cleaned daily with a brush, to remove the mud and organisms which collect on its outer surface. If this is not done, the organisms multiply and soon the filter pollutes the water instead of purifying it.

Most organisms can be killed by **boiling** the un-filtered water for 10 or 15 minutes, although a second boiling is needed in the case of some.

Purification from Dissolved Matter. — Filtration does not remove dissolved matter, and therefore does not soften hard water. For this latter purpose, washing powders are used in the laundry (see p. 504).

Pure water for chemical purposes is prepared by distillation and, in fact, liquids other than water are usually purified by the same process (Fig. 41). Dissolved solids remain in the flask (or boiler). The steam is condensed by cold water circulating in the jacket of the condenser. Freshly distilled water contains only gases dissolved from the air. Such water, however, quickly dissolves traces of glass or porcelain, so that the purest water is obtained by using quartz or platinum for the condenser tube and receiving vessel. Tin is the best of the less expensive materials.
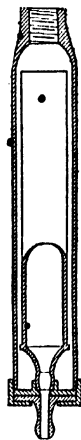
FIG. 40.

· **Chemical Properties of Water.** — Water is so very frequently used in chemical experiments in which it is a mere mechanical adjunct, that the beginner has difficulty in distinguishing the cases in which it has itself taken part in the chemical interaction. The four kinds of chemical activity which it shows should there-fore receive careful notice:

1. Water is a relatively stable substance.
2. It combines with many oxides, forming bases or acids.

3. It combines with many substances, chiefly salts, forming hydrates.

4. It interacts with some substances in a way described as hydrolysis. This property will not be discussed until a characteristic case is encountered.

Water a Stable Compound: Dissociation. — In the case of a *compound*, the first chemical property to be given is always, whether the substance is relatively **stable** or **unstable** (see p. 43).
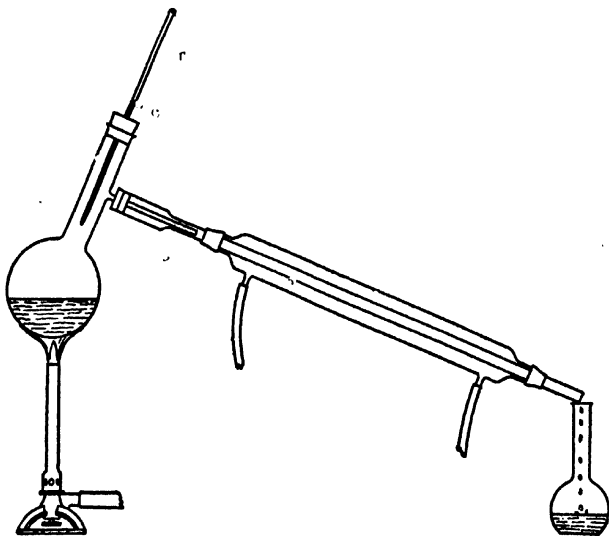
Fig. 41.

Usually the specification is in terms of the temperature required to produce noticeable decomposition. Thus, potassium chlorate gives off oxygen at a low red heat. Now, water vapor, when heated, is progressively decomposed into hydrogen and oxygen, yet at 2000° the maximum decomposition reaches only 1.8 per cent, and reunion occurs as the temperature is lowered. The two arrows in the equation indicate that the action may proceed in either direction — is **reversible**:

$$\text{Water vapor} \rightleftarrows \text{Hydrogen} + \text{Oxygen.}$$

A decomposition which is thus definitely reversible is called a dissociation.

Union of Water with Oxides. — 1. Sodium oxide unites violently with water to form sodium hydroxide. The slaking of quicklime is a more familiar action of the same kind:

Calcium oxide (56.07) + Water (18.016) → Calcium hydroxide
(74.086)
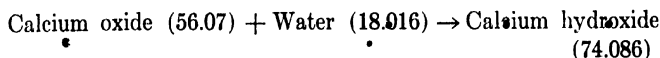
No other products are formed. The clouds of condensing steam produced in the second instance are due to evaporation of a part of the water by the heat produced in the formation of calcium hydroxide. The aqueous solutions of these two products have a soapy feeling, and turn red litmus (a vegetable extract) blue, and possess other properties which, as we shall see la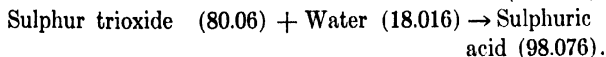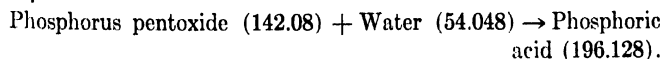ter, are characteristic of a class of substances called alkalies or **bases**. Very many hydroxides, which are of the same nature, for example ferric hydroxide and tin hydroxide, are formed so slowly by direct union of the oxide and water that they are always prepared in other ways. The oxides which, with water, form bases are called **basic oxides**.

2. Some oxides, although they unite with water, give **acids**, which are products of an entirely different character (see p. 61). Phosphorus pentoxide (p. 36) and sulphur trioxide are of this class and yield phosphoric acid and sulphuric acid. Such oxides are commonly called the **anhydrides** (Greek, *without water*) of their respective acids. They are called also **acidic oxides**:

Phosphorus pentoxide (142.08) + Water (54.048) → Phosphoric
acid (196.128).
Sulphur trioxide   (80.06) + Water (18.016) → Sulphuric
acid (98.076).

These two classes of final products are so different that we make the distinction the basis for classification of the elements present in the original oxides. The elements, like sodium and

iron, whose oxides give bases, are called **metallic elements**; those, like phosphorus, whose oxides give acids, are called **non-metallic elements.** The distinguishing words are selected because the division corresponds, in a general way at least, with the separation into two sets to which merely physical examination of the elementary substances would lead (see p. 23).

Hydrates. — Many substances unite with water to give compounds called **hydrates.** Thus if we take zinc sulphate (p. 62) and dissolve it in water and allow the excess of the latter to evaporate, the solid appears in long transparent crystals. When these are dried with blotting paper and heated in a test-tube, they give off a large amount of steam. The hydrate of zinc sulphate decomposes and leaves *anhydrous* zinc sulphate. The latter, when once more moistened, changes back into the hydrate.

Zinc sulphate + Water ⇌ Hydrate of Zinc sulphate.
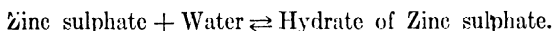
Many common chemicals are in fact such hydrates. Thus common blue-stone, used in gravity batteries, is a hydrate of cupric sulphate. When heated, it loses water and leaves the colorless, anhydrous cupric sulphate. These are cases of simple combination and decomposition.

That hydrates are regular chemical compounds (although of a more complex nature than any we have discussed in earlier chapters, being formed by the combination of *compound substances,* not of *elements*) is shown by the following two facts: (1) They contain definite proportions by weight of their constituent compounds. Thus blue-stone, when heated to give anhydrous cupric sulphate, always loses 36.1 per cent by weight of water, no more and no less. (2) A hydrate has physical properties entirely
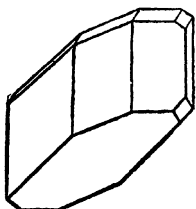
Fig. 42.

different from those of the water (or ice) and the other substance used in preparing it. Thus anhydrous cupric sulphate is a white substance, crystallizing in shining, colorless, needle-like prisms. Blue-stone, as its name implies, is

blue in color, and forms larger but much less symmetrical crystals (Fig. 42).

Efflorescence. — Some hydrates are so unstable that the water passes off, even at room temperature, when the hydrate is left in an open vessel. Thus crystals of washing soda (hydrate of sodium carbonate) crumble to powder (**effloresce**) *when not kept in a closed vessel:*

Sodium carbonate + Water ⇌ Hydrate of sodium carbonate.

If a crystal of a hydrate like this is placed in the barometric vacuum (Fig. 39, p. 75) a considerable vapor pressure of water is indicated, so that the tendency of the hydrate to decompose, when this vapor is allowed to escape, is easily understood. The pressure of water vapor in equilibrium with such hydrates, when partially dehydrated at ordinary temperatures, is found to be greater than the average pressure of water vapor in the atmosphere.

On the other hand, when anhydrous cupric sulphate and zinc sulphate, obtainable from the hydrates by heating only, are spread out in the air, they return slowly to the hydrated condition. They combine with the moisture in the air. The vapor pressure of water in the air is greater than the pressure of water vapor in equilibrium with these hydrates and their anhydrous products at ordinary temperatures. Calcium chloride absorbs water vapor (p. 71) because of its tendency to form a hydrate.

Reversible Chemical Actions. — The contrary effect upon an unstable hydrate of leaving the bottle open or closed, referred to above, deserves a moment's notice. When understood, it explains many things in chemistry. The hydration and dehydration are opposite directions of the same chemical change, and the condensed statements of the actions were written with the **double arrow** to indicate this (p. 82). When the bottle is closed the water vapor is unable to escape and recombines with the anhydrous particles as fast as other particles of the hydrate decompose. **A reversible action** therefore **cannot complete itself, i the products of the action are kept together and not allowed t**

separate. On the other hand, **a reversible action will go to com-pletion, if one of the products escapes,** as the water vapor does when the bottle is left open. This idea enables us to answer several interesting questions.

For example, why does steam decompose to the extent of 1.8 per cent at 2000°, but not any further? All its parts are alike and are therefore equally *capable* of decomposing. The answer is, because neither the oxygen nor the hydrogen is removed, or can easily be removed, from the steam, and so the completion of the decomposition is prevented by continual *recombination of these gases.*

When a reversible action has come to a standstill, we say that **equilibrium** has been reached. This means that two opposing tendencies are neutralizing one another's effects.

When will reversible actions go to completion? The products must be of such a nature that they *separate easily.* In practice this happens when *one is a gas or vapor,* like the water vapor coming from a hydrate, while the other is not. The *settling of one product as a precipitate,* while the other stays in solution, is, as we shall see (pp. 163-164), another common way in which the separation occurs.

When iron and water are heated in a *closed* vessel, the hydrogen and oxide of iron which are produced (p. 60) react with one another to give back water and iron:

Iron + Steam ⇌ Hydrogen + Magnetic oxide of iron.
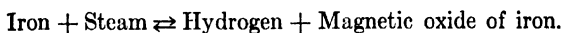
In a closed vessel we could never use this method for preparing any quantity of hydrogen. To prepare hydrogen by this action we must leave the tube open, and let the steam *sweep the hydrogen out.* This separates it effectually from the oxide of iron, and prevents the reversal of the action.

Devices depending on mechanical principles like this are continually used in chemistry for securing easy methods of preparing substances.

The reader can now answer for himself the question why we are able to prepare oxygen by heating mercuric oxide (p. 19), in spite of the fact that the action is reversible (p. 29).

Exercises. — 1. If 50 c.c. of hydrogen and 37 c.c. of oxygen are exploded in a closed tube, which gas remains and what volume of it is left?

2. Why do not bubbles of steam ordinarily form in water and rise through it at temperatures below 100°?

3. How many calories of heat would be required to change 5 grams of ice at 0° into steam at 100°?

4. How could one find out how much solid matter was dissolved in a sample of water?

5. Define: filtration, distillation, efflorescence, chemical equilibrium.

6. Name some familiar transitions (p. 74) from one physical state to another.

7. What evidence is there in the common behavior of ether and chloroform to show that these liquids have high vapor tensions?

8. What do you infer from the fact that alum and washing soda lose their water of hydration when left in open vessels, while gypsum does not?

9. Which fact shows most conclusively that hydrates are true chemical compounds?

10. Should you expect to find any difference, in respect to chemical activity, between the three forms of water? Have we had any experimental confirmation, or the reverse, of this conclusion (p. 60)?

CHAPTER VII

MOLECULAR WEIGHTS AND COMBINING WEIGHTS

As we have seen (p. 72), when the *volumes* occupied by sub-stances in the gaseous condition, rather than the weights, are taken as the basis of measurement, the combining proportions are *simple* and are expressible by *small whole numbers* (Gay-Lussac's law). This shows that there must be some relationship, *connected with chemical combination*, between the amounts of *different* substances contained as gases in equal volumes. It suggests that we might do well to take such amounts (weights of equal volumes) as the standard or unit quantities for chemical purposes. Now this is precisely what the chemist has found it in practice most convenient to do, and the present chapter deals with the units of material based upon comparing equal volumes.

Illustrations of Gay-Lussac's Law. — Let us first famil-iarize ourselves with the volume-measuring point of view in chemical actions. The following are a few observed facts, be-ginning with the union of hydrogen and oxygen already discussed (p. 71):

(1) Hydrogen (2 vols.) + Oxygen (1 vol.) → Steam (2 vols.).

(2) Hydrogen (1 vol.) + Chlorine (1 vol.) → Hydrogen chloride (2 vols.).

(3) Chlorine monoxide (2 vols.) → Chlorine (2 vols.) + Oxy-gen (1 vol.).

(4) Mercuric oxide (not volatile) → Mercury (2 vols.) + Oxygen (1 vol.).

(5) Phosphorus (1 vol.) + Oxygen (5 vols.) → Phosphorus pentoxide (1 vol.).

(6) Zinc (at 1000°, 2 vols.) + Sulphur (at 1000°, 1 vol.) → Zinc sulphide (not volatile).

It will be noted that in some cases, like (2), there is no change in the total volume. In others there is a shrinkage, as in (1) and

(5). In still others, like (3), where chlorine monoxide decomposes, there is an increase in volume. In (5), in order that all the materials may be gaseous, the whole experiment must be done at a very high temperature (and at some suitable pressure). In (4) the mercuric oxide itself does not become gaseous, but decomposes, so that its own relative volume cannot be given. In (6) the zinc and sulphur can be combined as vapors at 1000°. The product (zinc sulphide) will not remain gaseous at any temperature at which its volume could be measured, however, and so its volume is not recorded.

It must be kept constantly in mind that the law *applies to volumes in the state of gas or vapor only*. There is no rule about the proportions by volume required for the chemical combination of liquids and solids.

One can read these illustrations in different ways. For example: (1) A given volume of steam is formed by union of the same volume of hydrogen with half as great a volume of oxygen. (4) Mercuric oxide, when decomposed by heating, gives two volumes of mercury vapor and one volume of oxygen in every three volumes of the escaping gases. (5) One volume of phosphorus vapor, together with an equivalent quantity of oxygen, will give one volume of the vapor of phosphorus pentoxide, all being measured at the same temperature. In fact, whenever two vaporizable substances are amongst the factors and products of a chemical change, their volumes thus are either equal, or are to one another in the ratio of whole numbers.

Avogadro's Hypothesis. — We have seen (p. 51) that the physical behavior of matter, and particularly of gases, may be explained by the conception that matter is composed of molecules. Now Gay-Lussac's law is a chemical, and not merely a physical fact, yet the molecular hypothesis can explain it also.

Since matter is composed of molecules, a chemical action between two kinds of matter must consist really in an interaction of the molecules of each kind. Molecules of the two kinds must meet and they may then either *combine* to form a compound molecule, or they may *exchange* material in some fashion. Since equal volumes are often the exact quantities required for the

action, it appears most likely that **in equal volumes of different gases** (at the same temperature and pressure) **the numbers of molecules present are equal.** This addition to the molecular hypothesis was first suggested by an Italian physicist, Avogadro (1811). When two gases interact in equal volumes (like hydrogen and chlorine), one molecule of each is all that is required for a small sample of the change in question. Since two volumes of hydrogen are required to unite with one volume of oxygen (p. 71), clearly the interaction involves two molecules of hydrogen for every one of oxygen. Since two volumes of steam are produced, evidently the two molecules of hydrogen and one of oxygen yield two molecules of water.

This hypothesis of Avogadro helps us to a clearer notion of how these chemical changes take place. The idea that all gases contain equal numbers of molecules in equal volumes also explains why *all* gases behave alike when subjected to equal pressures, or to equal changes in temperature (Boyle's and Charles' laws, p. 46). No facts which conflict with this hypothesis are known, and all the known facts confirm it. Hence, Avogadro's hypothesis has been accepted by chemists, and since 1858 has been the keystone of chemical theory.

The Standard or Unit Volume. — The volumes in the fore-going paragraphs are simply relative, and the statements are true of gaseous volumes of any actual dimensions (large or small), provided only they bear the proper *relationship*, such as 2 : 1, 1 : 1, or 1 : 5, in each case. An actual value has been chosen, however, for the volume which is the standard or unit in chemistry. This is the volume occupied by 32 grams of oxygen, which is **22.4 liters** at 0° and 760 mm. This volume is equal to that of a cube about 11 inches in height (Fig. 43). At other temperatures and pressures this volume, in order to contain the same amount of material, alters
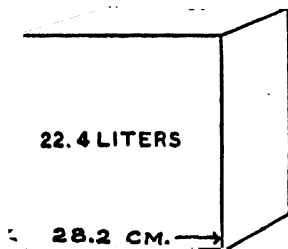
22.4 LITERS

28.2 CM.

Fig. 43.

•its value, in accordance with the laws of Boyle and Charles (p. 46). The reason for selecting this particular volume will be readily seen, so soon as we shall have presented and discussed in detail the actual weights of various materials which fill it.

Consequences of Avogadro's Hypothesis — Molecular Weights. — Equal volumes of the *same* gas (at the same temperature and pressure) have equal weights. But equal volumes of *different* gases have different weights. The differences are often very great. Thus, bulk for bulk, oxygen is sixteen times as heavy as hydrogen, and mercury vapor one hundred times as heavy. Now, if equal volumes of different gases contain equal numbers of molecules, these differences must be due to the differing weights of the several kinds of molecules. Thus, measuring the weights of equal volumes of different gases will give us the relative weights of their molecules. For example, since 22.4 l. of oxygen weigh 32 g., while the same volume of hydrogen weighs 2.016 g. and of water vapor 18.016 g., and these are the weights of equal numbers of molecules, the individual molecules must differ in weight in the ratio 32 : 2.016 : 18.016. These are the relative weights of the three kinds of molecules. In chemistry the weights in grams of 22.4 l. (at 0° and 760 mm.) of various gases are called the **molecular weights** of those gases. The unit volume, 22.4 l., is called the **gram-molecular volume** (G.M.V.).

The number of molecules actually contained in the G.M.V. has been determined by several independent methods, the agreement of the results obtained furnishing very strong support for the validity of the molecular hypothesis. The value at present accepted as most accurate is that of Millikan, 6.06×10^{23}*. It is of importance that the student should obtain some idea of the significance of this stupendous number, in order to appreciate more clearly the detailed discussion of the properties of gases in an earlier chapter (pp. 51-56). Imagine a G.M.V. of a gas at 0° and 760 mm. to be divided equally among the inhabitants of the

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* This is the method used in physics and chemistry to express numbers so large as to be cumbrous and incomprehensible if written in the ordinary way. It means that the unit is to be followed by the number of zeros indicated by the exponent. In this case, the quantity written out at length would be 606.000,000,000,000,000,000,000.

United States (say 110,000,000). Each person would receive about one-fifth of a cubic millimeter as his share. Imagine, further, that the market price of a million molecules of this gas was one cent. Few of the recipients would think it worth while to cash in their microscopic sample; those doing so, however, would benefit to the extent of over 50 million dollars!

A common question is: Do not molecules of different substances differ in size, and will not the numbers required to fill the G.M.V. therefore be different? The answer is that the molecules are all so small compared with the spaces between them (at 760 mm.) that the distances from surface to surface are practically the same as from center to center. A G.M.V. of oxygen, when liquefied, gives less than 32 c.c. of liquid oxygen, or less than $\frac{1}{700}$ of the volume as gas. It is only when gases are so severely compressed that the nearness of the molecules to one another approaches that found in the liquid condition that the effects of the bulk of the molecules become conspicuous, and a difference in the behavior of different gases is noticeable. But in the work discussed in this chapter, pressures over one atmosphere are intentionally avoided.

Molecular Weight, Measurement of. — The molecular weight is *measured* by weighing any convenient volume of the gas (say 200 c.c.), and calculating by proportion the weight of 22.4 l. If the gas or vapor was not measured at 0° and 760 mm., the measured volume must be reduced by rule to standard conditions before the weight of 22.4 l. is calculated.*

For example, 190 c.c. of a gas at 0° and 760 mm. weigh 1.23 g. If x be the weight of 22.4 liters ($= 22{,}400$ c.c.),

$$190 : 1.23 :: 22{,}400 : x \ (= 145 \text{ g.}).$$

Again, 210 c.c. of a vapor at 100° and 743 mm. weigh 1.12 g. This volume at 0° and 760 mm. would become:

* In practice, owing to the fact that Boyle's and Charles' laws do not describe the behavior of any known gas *exactly* (they apply only to a "perfect" gas), certain additional, small corrections have to be applied when very precise values are required (see p. 55). It may be noted that, in order to make the fundamental significance of the numerical data presented in this chapter immediately intelligible to the beginner, all of the gases here considered have been *assumed* to be "perfect." The actual experimental values differ only very slightly from those given.

$$210 \times \frac{273}{373} \times \frac{743}{760} = 150.3 \text{ c.c.}$$

and

$$150.3 : 1.12 :: 22{,}400 : x \; (= 167 \text{ g.}).$$

The Weights Filling the Unit Volume, 22.4 Liters. — The following table contains a few sample substances, and gives the weight (in grams) of each which, in the gaseous condition, at 0° and 760 mm., occupies the cube — 22.4 liters. In the cases of compound substances, like water, we have given also the weights of the constituent elements which together make up the total weight of the compound filling the unit volume:

WEIGHTS OF GASES IN 22.4 LITERS (AT 0° AND 760 MM.).

Substance	Total wt.	Wt. oxygen	Wt. hydrogen	Wt. chlorine
Oxygen	32	32	....	....
Water	18.016	16	2.016	....
Hydrogen	2.016	....	2.016	....
Hydrogen chloride ...	36.468	....	1.008	35.46
Chlorine	70.92	....	....	70.92
Chlorine monoxide ..	86.92	16	....	70.92

The first column ("Total wt.") gives the number of grams of each substance occupying, as a gas, 22.4 liters at 0° and 760 mm. This, as we have explained above, is the **molecular weight of that substance**. In the case of water, which is a liquid at room temperatures and pressures, a known volume of *steam* is weighed. The volume is reduced by rule to 0° and 760 mm., and the weight of 22.4 liters is calculated from the reduced volume and the measured weight.

Unit or Standard Weights of the Elements. — Let us now examine the weights of the constituent elements making up a cubeful of each substance, as shown in the last three columns of the above table. We must first be sure we understand what these numbers are. They are combining proportions, such as we have given on previous occasions (*e.g.*, pp. 19, 23, 36). They are equivalents (p. 64). We can use them in our condensed form for representing chemical changes:

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Oxygen (16) + Hydrogen (2.016) → Water (18.016).

· Hydrogen (1.008) + Chlorine (35.46) → Hydrogen chloride (36.468).

‣ We observe at once that the weights in the oxygen column, or the chlorine column, for example, are not identical. There was no reason to expect that they would be alike, since different substances differ in composition. But we do observe that *the weights of any one element are all exact multiples of the smallest number in its column, either by unity or some other whole number.* Thus. for hydrogen, the weights are: 2.016, 2.016 and 1.008. The unit weight of water contains *exactly* the same weight of hydrogen as does the unit weight of hydrogen itself, and *exactly* twice as much as does the unit weight of hydrogen chloride. Similar relations hold in the oxygen and chlorine columns. This is a very surprising, natural fact, and, better still, one for which we instantly perceive a use. This fact greatly simplifies our task of finding some way of expressing the compositions of substances in a simple manner. The fact does not apply to a few compounds only. If our table had included all the hundreds of compounds of chlorine (for example) which are capable of being converted into vapor, we should have found, indeed, many multiples of 35.46 larger than the two units (70.92) in chlorine monoxide, but no number smaller than 35.46 and none which was not a multiple of 35.46 by a whole number. Clearly we shall find it convenient to accept 35.46 as the unit or standard weight of chlorine for expressing the compositions of its chemical compounds. Its use will enable us to state the exact composition of any given compound by simply *giving the whole number* (1, 2, 3, etc.) by which the *basal weight* 35.46 *is to be multiplied* in the given case.

Similarly, we take 1.008 as the unit weight of hydrogen and 16 as the unit weight of oxygen. By including volatile compounds of other elements in our investigation, we can similarly pick out the most convenient unit for each element.

The Law of Combining Weights. — The **general fact** which we have developed in the preceding section is known as the law of combining weights: **All the proportions in which the elements combine with one another may be represented by a set of numbers**

(one for each element) **or by multiples of these numbers by whole numbers.**

The following table presents the results obtained from a larger number of substances. It should be carefully studied.

| Substance | Molec- ular Weight | Combining Weights of Constituent Elements. | | | | | |
		Hydrogen	Chlorine	Oxygen	Phosphorus	Carbon	Mercury
Hydrogen chloride	36.468	1.008	35.46	.....	.....	.....	.....
Chlorine dioxide	67.46	.....	35.46	32	.....	.....	.....
Phosphorus trichloride ..	137.42	.....	106.38	.....	31.04	.....	.....
Phosphorus oxychloride .	153.42	.....	106.38	16	31.04	..0..	.....
Phosphorus pentoxide ...	284.16	.....	.....	160	'24.16	.....	.....
Phosphine	34.064	3.024	.....	.....	31.04	.....	.....
Water	18.016	2.016	.....	16	.....	.....	.....
Methane	16.037	4.032	.....	.....	.....	12.005	.....
Acetylene	26.026	2.016	.....	.....	.....	24.010	.....
Ethylene	28.042	4.032	.....	.....	.....	24.010	.....
Formaldehyde	30.021	2.016	.....	16	.....	12.005	.....
Acetic acid	60.042	4.032	.....	32	.....	24.010	.....
Mercurous chloride	236.06	.....	35.46	...l.	.....	.....	200.6
Mercuric chloride	271.52	..a..	70.92	.....	.....	.....	200.6

The Case of Non-volatile Compounds. — The same elements enter also into many compounds which are not volatile. But the unit weights of such elements, determined by the use of volatile compounds, are found (by using multiples, when necessary) to express the composition of the involatile compounds also.

For example, the unit weight for oxygen (16) and that for mercury (200.6), both formed by studying volatile compounds, are found correctly to express the composition of mercuric oxide (p. 23), which is not volatile.

In the cases of some elements no easily vaporizable compound is known, and the unit weight cannot be determined by the present method. In such instances, an entirely different way of obtaining the value of the unit weight is employed (see p. 104).

Law of Multiple Proportions. — We have already met with several instances in which two elements combine in more than one proportion by weight, and form therefore more than one com-

pound. Thus two oxides of iron (p. 36) and two oxides of sul-
phur have been mentioned, and several compounds of carbon
and hydrogen are included in the table on p. 95. This general
fact was discovered before the law of combining weights (p. 94)
had been formulated, and constitutes, when quantitatively ana-
lyzed, a particular case of this law. It was discovered by Dalton
(1804), and was embodied by him in a statement known as the
law of multiple proportions, which ran somewhat as follows:
**If two elements unite in more than one proportion, forming two or
more compounds, the quantities of one of the elements, which in the
different compounds are united with identical amounts of the other,
stand to one another in the ratio of integral numbers, which are
usually small.**

The two chlorides of mercury in the table on p. 95 illustrate
the law. Mercurous chloride contains mercury 200.6 and chlorine
35.46, and mercuric chloride mercury 200.6 and chlorine 70.92.
Thus the quantities of chlorine united with identical amounts of
mercury (namely, 200.6 parts) stand in the ratio 35.46 : 70.92,
or 1 : 2.

Exercises. — 1. State the change which takes place in the
total volume of the gases or vapors in each of the six actions
mentioned, p. 88.

2. If 1 liter of nitrogen at 0° and 760 mm. weighs 1.251 g.,
what is the molecular weight?

3. Calculate the molecular weight of a gas, 200 c.c. of which
at 0° and 760 mm. weigh 2.1 g.

4. Find the molecular weight of a gas, of which 250 c.c. at 18°
and 752 mm. weigh 2.5 g. (p. 92).

5. The weight of 1 c.c. of sulphur dioxide is 0.00286 g. at 0°
and 760 mm. What is its molecular weight?

6. The density of a gas, air $= 1$, is 2.3. What is its molecular
weight?

7. By the use of combining weights, show how the two oxides
of iron (pp. 13, 36) illustrate the law of multiple proportions.

8. Show, in a similar way, how the two oxides of sulphur
(pp. 36, 83) illustrate the same law.

CHAPTER VIII

MANY different values for each element would satisfy the law of combining weights as stated on p. 94 above. We could arbitrarily assign any number we pleased to oxygen (or to any other element, for that matter), and call it the combining weight, provided we changed the quantities of other elements uniting with our standard element correspondingly. The particular values chosen as units in chemistry, however, fulfil an *additional condition* which fixes the value in each case, absolutely. We always employ for our combining weights (as in the tables on pp. 93 and 95) **those weights of the elements which are found in the molecular weights of their various compounds.**

Atomic Weights. — The combining weights adopted by the chemist are consequently all based upon the *gram-molecular volume* (p. 90); we have for each element a definite number, or a multiple of this by a whole number, which expresses the weight in grams of that element found in 22.4 liters (at 0° and 760 mm.) of the vapor of its volatile compounds. **The smallest weight of an element found in 22.4 liters (at 0° and 760 mm.) of the vapor of any volatile compound of that element is called its atomic weight.** The amounts of the element in 22.4 liters of other compounds are all either the same amount or multiples thereof by a whole number.

. Since we employed a given weight of oxygen as our standard in fixing the gram-molecular volume (p. 90), and since the smallest weight of oxygen found in the gram-molecular volume of the vapor of any volatile compound of oxygen under standard conditions is 16 grams (p. 94), it will be seen that **the atomic weights of all elements are based upon the standard: oxygen = 16.**

From the data presented in the tables on pp. 93 and 95, the following atomic weights may also be deduced:

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Hydrogen   ˙ 1.008 Phosphorus   31.04 ˙Mercury   200.6
Chlorine   ˙ 35.46 Carbon   12.005

A complete list of the atomic weights ior all the known elements
is given in a table inside the rear cover of this book. These
numbers will hereafter be in constant use.   ˙ ⁻

The Significance of Atomic Weights. The Atomic Theory.
— To *explain* the law of combining weights it was˙again found
necessary to use the third kind of explanation (p. 26), namely
the making of an hypothesis. The details of *how* two substances
combifie cannot be seen, so chemists had to *imagine* some details
which would account for the possession of an individual unit
weight by each element. If oxygen *is ultimately composed of
exceedingly minute indivisible particles*, which are *all alike in
weight*, and all other elements are of the same′nature, except that
*the weight of the ultimate particle of each kind of element is
different*, we have the basis of an explanation. We have to sup-
pose, further, that, when elements combine, *the particles adhere in
pairs or groups, cs wholes, and are never broken*. In this way
the *ultimate particle* of each variety .of elementary matter will
have a definite, unchangeable weight, which will be one of its
fixed properties. If the relative weights of the *ultimate particles*
of hydrogen, chlorine, oxygen, phosphorus, carbon and mercury
are in the proportion of the smallest combining numbers in the
table on p. 95, namely: 1.008 : 35.46 : 16 : 31.04 : 12.005 : 200.6,
the whole situation becomes clear. Chemical union in every case
must consist, in detail, in the union of the particles of the con-
stituent elements to form the particles of the compound.

For each particle of hydrogen chloride, *one particle each* of
hydrogen and chlorine is required. For each particle of water,
where the proportion of oxygen to hydrogen is 16 : 2.016, evi-
dently one particle of oxygen and *two* particles of hydrogen are
necessary. Varying, intermediate proportions are impossible,
because the particles of the elements are permanent, are never
broken, and combine as wholes, and in a uniform way through
the mass. The only possible variation would be to take different
relative numbers of the particles — for example, two of oxygen
to two of hydrogen $(2 \times 16 : 2 \times 1.008)$. But this product

would have a different composition from water, and would not
be water. This compound, with the double proportion of oxygen,
is indeed known (it is hydrogen peroxide), and is the only other
known compound of these two elements.

This theory fully explains why the combining proportions of
each element, in different compounds, can always be expressed
by a fixed, unit number (which represents the weight of the
ultimate particle of that element), multiplied, when necessary,
by a whole number (representing the number of particles of
the element required to form a particle of the compound in
question).

This explanation was first offered by Dalton, a schoolmaster
of Manchester, in 1802. Borrowing an idea from the speculations
of the Greek philosophers, he called the *ultimate particles of ele-
ments* atoms (Greek, *not cut,* or *not divided*). With their as-
sistance he developed the atomic theory as outlined above. For
ong it remained an hypothesis, or sort of guess. Recently, how-
ver, we have obtained independent proof that atoms are real
(see pp. 720-730), and we even know something of the *inside*
structure of atoms.

Distinction between Atoms and Molecules. — At this point it
s profitable to attempt to remove any confusion which the
tudent may have in his mind with respect to the two concep-
ions of *atoms* and of *molecules,* as applied to elementary sub-
tances such as oxygen. In the kinetic-molecular hypothesis we
lefined the molecules of a gas as exceedingly small particles, all
like in mass, separated from one another and in rapid motion.
n the atomic theory, atoms are defined as the ultimate particles
f an element, also all alike in mass, by the co-ordination of
vhich with the ultimate particles of other elements compounds
f definite composition are produced.

That the atom and the molecule are not *identical* in the case
f gaseous oxygen will be evident from the fact that, in the de-
velopment of molecular weights, we employed oxygen $= 32$ as
ur standard, while for the atomic weight of oxygen we have
rrived at the value 16. In other words, while 22.4 liters of oxy-
en at 0° and 760 mm. weigh 32 grams, volatile compounds of

oxygen (such as phosphorus oxychloride and water) are known, which contain as gases only 16 grams of oxygen in 22.4 liters (reduced to 0° and 760 mm.). Now equal volumes of all gases under the same conditions contain equal numbers of molecules (Avogadro's Law). Hence we are forced to the conclusion that the weight of oxygen in a molecule of oxygen must be twice the weight of oxygen in a molecule of vaporized phosphorus oxychloride or water. But the molecules of these compounds must contain at least one atom of oxygen, since atoms are indivisible. Consequently the molecule of oxygen in the gaseous state must contain at least two atoms of oxygen. We have no reason for believing that it contains more than two, since we know of no volatile compounds which contain less than 16 grams of oxygen in their gram-molecular volume. The molecule of oxygen is therefore regarded as **diatomic**, or as consisting of two atoms in intimate conjunction.

This example, to which we shall return later (see p. 120), will be sufficient for the present to indicate the essential point of distinction between atoms and molecules. The **atoms** are the *ultimate particles* of an element, but the element in its free state does not *necessarily* exist in its ultimate state of subdivision. In some cases we shall find that it does, but in most of the common gaseous elements (such as hydrogen, oxygen and chlorine), the atoms are held together in pairs to form molecules. With some elements in the gaseous state, the molecules are even more complex units. In the definition of a molecule, although we recognize that it is an exceedingly small particle, we do not pay any attention at all to the question of further divisibility. The **molecule** is a unit which is now based directly upon experimental data — in a perfect gas at 0° and 760 mm., 6.06×10^{23} molecules occupy 22.4 liters (see p. 91). Whether each of these 6.06×10^{23} discrete particles existent in the gram-molecular weight of a gas is further divisible or not is of no immediate significance. Each molecule may contain only one atom, or it may consist of a group of atoms. That is something which will depend upon the particular substance under examination, but the behavior of the gas, so far as laws founded on molecular relationships are concerned, will be exactly the same in all cases.

• When we come to compounds, of course, the distinction between atoms and molecules is much more evident.

The molecule is here necessarily a complex unit, built up by the association of the atoms of the constituent elements into definite groups. Each group contains a fixed *integral* number of the atoms of each element, and the *proportions* in which these integers stand in any given compound may be calculated from the composition of the compound by weight (p. 111). To find the actual molecular unit (*i.e.*, the *absolute* number of atoms of each element contained in the molecule) a molecular weight determination is necessary, as will be illustrated in a later section (p. 118).

Although in the above discussion, as well as elsewhere, we have emphasized the fact that atoms are not divided into parts, this must not be taken to mean that atoms are quite incapable of being disrupted. It means only that in ordinary chemical changes, the atoms combine and separate as wholes. Indeed, we now know that the atom of radium (compare p. 723) gives off atoms of helium, and leaves an atom of lead, and that the atoms of one or two other elements *disintegrate* in a similar way. Rutherford's recent success in breaking up certain more familiar kinds of atoms has also been mentioned in a previous connection (p. 21).

Why was 22.4 Liters Chosen as the Unit Volume? — This point is now ripe for discussion. It is clearly advantageous to employ a standard gram-molecular volume of such dimensions that no element shall receive an atomic weight smaller than unity. At first sight, indeed, it would seem self-evident that we ought to choose, for our own convenience, a unit volume based on a smallest unit weight of *exactly* 1. Now hydrogen is the element which enters in the smallest proportions into chemical combination, and we have seen that in 22.4 l. of some compounds there is as little as 1.008 g. of this element (see table, p. 93).

If a slightly smaller gram-molecular volume (22.2 l.) had been chosen, hydrogen would possess an atomic weight of *exactly* 1. Why was not, it will be asked, this volume selected instead of 22.4 l. as our standard? It was, in fact, at one time the standard, the atomic weight of oxygen being then about 15.9 and the atomic

weights for all of the other elements being correspondingly re-
duced. The transfer to the present scale of atomic weights, based
on oxygen $\doteq$ 16, was made for a purely practical reason: because
of the greater *activity* of oxygen (see p. 43), the exact determina-
tions of the combining proportions of most other elements are
generally given by experiment on an oxygen, not on a hydrogen,
basis. It so happens, also, that the majority of atomic weights
on the scale oxygen = 16 are very close to whole numbers (see
table), an aid to calculations being thereby afforded which does
not exist under the standard hydrogen = 1. Recent work on the
"complexity" of elements, it may be added, has given further
justification of our choice of the oxygen standard here adopted
(see pp. 728-729).

The accepted scale is, therefore, that of 32 for the molecular
weight of oxygen gas; 22.4 l. (the volume of 32 g. of free oxygen)
for the chemical unit of volume; and 16 for the atomic weight of
oxygen in compounds containing that element. The unit weights
of all the other compounds and elements are based upon this scale.
Of course, multiplying or dividing all the atomic weights by any
number, whole or fractional, would not affect their scientific ac-
curacy. The choice of scale is merely a matter of convenience.

In physics there is one unit of weight, the gram, for all kinds
of matter. Is it the case that in chemistry a different unit of
weight is employed for each element? This is the exact situation,
and it is one peculiar to chemistry. It does not represent an
arbitrary decision of the chemist, however. It is due to the fact
that the atoms of any one element have the same weight, but
that the atoms of different elements have different weights.

Determination of Atomic Weights. — To avoid a common
error, the reader should note once more that to learn the atomic
weight of an element, we do **not** measure the molecular weight
of the simple substance. The molecular weight of the elementary
substance may be a multiple of the atomic weight, and we find
out whether it is such a multiple only after the atomic weight
has been determined. The atomic weight is the unit weight used
in compounds, and can be ascertained only by a study of com-
pounds. The molecular weight of the free element gives us only

a value which we know must be a multiple of the atomic weight, by 1 or some other integer. Mol. Wt. $=$ At. Wl. $\times$ x, where x is 1 or some other integer.

The most general method for the determination of atomic weights is clearly indicated in the definition of the atomic weight of an element as the smallest of the weights of the element found in the molecular weights of all its volatile compounds, so far as these have been examined.

It is hardly necessary to add that the atomic weights, found as described above, are equally serviceable in expressing the compositions of compounds of the same elements which are *not* volatile. The atoms in non-volatile compounds are identical in properties with the atoms of the same elements in volatile compounds. If an element gives no volatile compounds, another method of fixing its atomic weight must be employed (see p. 104 below).

Many chemists have contributed to the determination and revision of the atomic weights. The Swedish chemist Berzelius devoted many years to the accurate measurement of combining proportions. Stas, a Belgian (1860–1870), made a number of determinations with great exactness. Morley's (1895) value for the combining proportions of hydrogen and oxygen alone represented several years of work. T. W. Richards of Harvard University has recently carried many of the values to a higher degree of accuracy.

In one important detail the original theory of Dalton has lately been found to be inaccurate, namely in postulating that atoms of the same element are all alike in weight. Many elements, in point of fact, have been shown to contain *two or more distinct kinds of atoms, identical in their general chemical properties, but differing essentially in mass.* Such varieties of the same element are called *isotopes.* Thus *chlorine* consists of an intimate mixture of two isotopes of mass exactly 35 and of mass exactly 37, in such proportions that the *average* atomic weight is 35.46. This point will be discussed more fully in a later chapter (see p. 728). At the present stage it will suffice to mention that, inasmuch as all naturally-occurring chlorine has exactly the same average atomic weight, and no method for the large-scale

separation of the two isotopes has yet been devised, we may continue to use, in our ordinary chemical work, 35.46 as the atomic weight of chlorine and may still regard our fundamental chemical laws, such as the law of definite proportions (p. 23), as valid in all of their practical applications.

Dulong and Petit's Law, an Alternative Means of Determining Atomic Weights. — It was first pointed out (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the atomic weights of the elements were multiplied by the specific heats of the simple substances in the solid condition, the products were approximately the same in all cases. In other words, the specific heats are inversely proportional to the magnitudes of the atomic weights. The following table, in which round numbers have been used for the atomic weights, shows that the product lies usually between 6 and 7, averaging about 6.4:

Element.	Atomic Wt.	Sp. Ht.	Product.	Element.	Atomic Wt.	Sp. Ht.	Product.
Lithium	7	0.94	6.6	Iron	56	0.112	6.3
Sodium	23	0.29	6.7	Zinc	65.4	0.093	6.1
Magnesium	24.3	0.245	6.0	Bromine (Solid)	80	0.081	6.7
Silicon	28.3	0.16	4.5	Gold	197	0.032	6.3
Phosphorus				Mercury (Solid)	200	0.0335	6.7
(Yellow)	31	0.19	5.9	Uranium	238.5	0.0276	6.6

Another way of expressing this law will give it greater chemical significance. The specific heats are the amounts of heat required to raise one gram, that is one *physical* unit, of each element through one degree. When we multiply this by the atomic weight, we obtain the amount of heat required to raise one gram-atomic weight of the element, that is, one chemical unit, through one degree. The values of this product (the "atomic heat") are approximately equal. Since there are equal numbers of atoms in one gram-atomic weight of each element, it follows that: **Equal amounts of heat raise equal numbers of atoms of all elements in the solid state through equal intervals of temperature.**

The law of Dulong and Petit, formerly regarded as purely empirical, is now theoretically established, and may be **used for fixing the atomic weight of an element of which no volatile com-**

pounds are known. We can always measure that weight of such
an element which combines with *one atomic weight of another
element*. Since the elements concerned must combine atom for
atom, or in some simple ratio such as 1 : 2 or 2 : 3, it follows
that the weight found is either the atomic weight or some mul-
tiple or submultiple of it by a whole number. When, therefore,
we multiply this weight by the specific heat, we discover at once
whether the product is 6.4 or some simple fraction or multiple of
this number. For example, suppose the atomic weight of calcium
to be unknown. We find by analysis (or by means of equivalents,
see p. 64) that calcium chloride contains 20 parts of calcium
combined with 35.46 parts (the atomic weight) of chlorine. Now
the specific heat of solid, metallic calcium is 0.170. This number
multiplied by 20 gives as the product 3.4. Evidently, therefore,
the atomic weight is not 20, but 40, for the product, 6.8, then
agrees fairly well with the average for other elements.

The **Properties of Solids.** — The fact, noted in the preceding
section, that equal amounts of heat raise equal numbers of atoms
of all elements in the solid state through equal intervals of tem-
perature leads us to consider at this point the general structure
of matter in the solid state. The gaseous and liquid states of
matter have already been discussed in the light of the kinetic-
molecular hypothesis (pp. 51, 77), and the present section there-
fore completes our examination of the relations between the
structure and behavior of matter.

The **Properties of Solids.** — True solids are sharply distin-
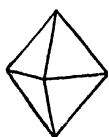guished from liquids by their *crystalline forms* (Figs. 44–48, see
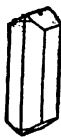
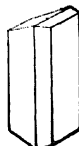| Fig. 44.	Fig. 45.	Fig. 46.	Fig. 47.	Fig. 48.
Octahedron	Square Prismatic	Rhombic	Monosymetric	Asymmetric
(Alum)	(Zircon)	(Niter)	(Gypsum)	(Potassium dichromate)

also pp. 4, 17 and 84) which possess definite planes of cleavage
and by their behavior towards light and X-rays give further evi-

dence of *regular structure.** Substances such as glass, which do not exhibit any specific crystalline form, although commonly called solids, are strictly speaking still in an extremely viscous liquid state. In such substances, as in liquids and gases, the cohesive forces between adjacent molecules are exercised equally in all directions, with the result that the molecules are all in haphazard, unordered positions relative to one another and no particular arrangement of particles in space can persist. Substances of this character are therefore called **amorphous** (Greek, *without form*). In crystals, on the other hand, since each substance shows an individual structure, the forces between adjacent particles must be exercised *in definite directions.*

By using crystals of different substances as X-ray gratings (see p. 725), W. H. and W. L. Bragg (1914) have been able to show that crystals are composed of *particles arranged in rows,* the spacing of these rows with respect to one another determining the geometrical form of the crystal. They have also succeeded in proving that the particles, which so arrange themselves in definite patterns in crystals, are *not* molecules, much less aggregates of molecules, but *atoms* of the constituent elements of the substance. Thus when common salt (sodium chloride), which crystallizes in cubes, is examined by reflecting X-rays from an appropriate plane, it is found to consist of alternate rows of *sodium atoms* and *chlorine atoms,* the rows being arranged in space in such a way as to build up a cubical structure. The framework of a unit cube of sodium chloride is shown in Fig. 49. The actual length of a side of this cube is approximately only one hundred millionth of an inch! However, by imagining other cubes to be
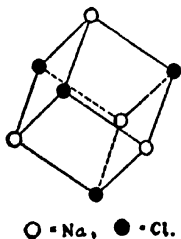
O • Na, ● • Cl.

Fig. 49.

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* Formerly chemists gave much attention to the classification of crystals according to their degree of symmetry, and some of the various systems included in this classification are illustrated in the above diagrams (Figs. 44-48). Exterior crystal form is a specific property which is still of great importance in the *recognition* of a substance, and a whole distinct science —crystallography—is devoted to its study. In chemistry itself, however, interest is now centered upon the *interior arrangement* of the atoms which constitute the crystal lattice, as indicated in Figs. 49 and 50.

packed all round' this, with atoms of sodium and of chlorine placed at their alternate corners, the reader will obtain for himself an idea of the ultimate structure of a crystal of common salt. Most sub-
stances crystallize in
less simple geomet-
rical forms and con-
sequently possess a
much more complex
structure. The
framework of the
carbon atoms in a
diamond, for exam-
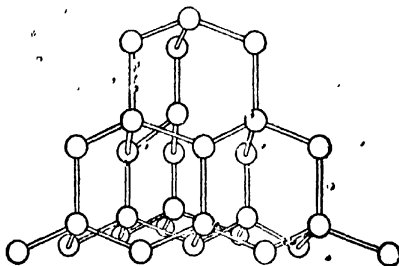ple, is indicated in
Fig. 50.

FIG. 50.

In a substance in the crystalline state, therefore, definite molecular units no longer exist. Thus, in sodium chloride, no sodium atom can be said to be combined *specifically* with any one chlorine atom. It is, instead, imprisoned by a number of chlorine atoms, stationed at definite intervals around it, and among these chlorine atoms its combining forces must be regarded as impartially dispersed. Very powerful forces, it will be evident, must be called into play in order to constrain the separate atoms in a crystal to retain their regular positions with respect to one another. The nature of such forces will be discussed in a later chapter (see pp. 730-731).

The resistance offered by the atoms in a crystal to forcible changes of position is shown by the very low *compressibility* of matter in the crystalline state. Nevertheless, some degree of *motion* of the particles must still persist, since many crystalline substances show a measurable vapor pressure. Some vapors, indeed (*e.g.,* phosphorus, iodine), can be condensed directly to crystals without passing through the intermediate liquid state.

The results of X-ray work indicate that this motion of the atoms of a crystal consists of *rapid vibrations* about a mean position. Atoms vibrating violently at the surface are evidently exposed to the risk of breaking away altogether, after which they combine to form molecules of vapor. Similarly, molecules of

vapor striking the crystal surface may stick thereto, their constituent atoms arranging themselves in a continuation of the crystal pattern. Equilibrium relations between crystals and vapor resemble closely, therefore, those between liquid and vapor discussed in an earlier chapter (pp. 77-79), to which reference should here be made.

Exercises. — 1. If 100 liters at 0° and 760 mm. had been chosen for the gram-molecular volume, what would be the atomic weight of oxygen?

2. Express in terms of atomic weights the composition of cupric oxide (p. 39).

3. To raise the temperature of 1000 grams of an elementary substance in the solid state 1°, 75 calories (p. 72) are required. What is the atomic weight of the substance?

4. What is the number of atoms in a gram-atomic weight of an element?

5. Magnesium oxide has been shown to consist of atoms of magnesium and oxygen arranged in a simple cubic structure, exactly similar to that shown for sodium chloride in Fig. 49. Given that the density of magnesium oxide is 3.5, calculate the distance between the centres of adjacent atoms (Use exercise 4).

CHAPTER IX

*SYMBOLS, FORMULÆ AND EQUATIONS

HAVING developed in detail the ideas of molecular and atomic weights, we are now in a position to indicate the important practical applications of these ideas in chemistry.

Although the method of selecting atomic weights involves rather complex reasoning, these weights repay the trouble, because they represent the relative weights of the atoms themselves. They are thus much more valuable in helping us to understand chemical behavior and in enabling us to classify the phenomena of chemistry than would be any other units of weight we might have chosen.

Symbols and Formulæ. — One self-evident use for the atomic weights is in stating the compositions of compounds. To make the statement as simple as possible, **symbols**, first used by Berzelius, **represent the atomic weight of each element.** Thus, H stands for 1.008 parts, or 1 atom, of hydrogen, and O for 16 parts, or 1 atom, of oxygen. When several elements have the same initial letters, another letter is added: C for one atomic weight of carbon, Ca for one atomic weight of calcium, Cl for 35.46 parts of chlorine. When the names of the elements are not alike in all languages, the symbol is frequently based on the Latin name, as Fe for iron (*ferrum*) and Pb for lead (*plumbum*), or on the German, as K for potassium (*kalium*). The symbols are international. A complete list of the symbols employed in chemistry is included in the table of atomic weights printed inside the back cover of this book.

The composition of any compound can thus be stated by setting down the necessary symbols, together with the whole numbers, if different from unity, by which the atomic weights are

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multiplied. The result is a **formula.** For example, magnetic oxide of iron contains iron 167.52 and oxygen 64 parts (p. 60). This is equivalent to iron 3×55.84 and oxygen 4×16. This again is equivalent, in symbols, to $3 \times \cdot$Fe and $4 \times O$. The formula is written Fe_3O_4. Ferrous sulphide is a simpler case: iron 55.84 and sulphur 32.06, or in symbols, FeS. The reader should now examine the condensed statements of various reactions included in the preceding chapters, and work out the formula of each compound, and write it in the margin.

It must be noted particularly that the *formula,* to be consistent, *must represent also the total weight of the unit quantity of the substance* (wt. of 22.4 l.) in the gaseous state. Thus, HCl $(1.008 + 35.46 = 36.468)$ is correct, since 36.468 g. is the amount filling the cube. Again, the formula for oxygen gas itself must represent 32 g. $(= 2 \times 16)$, the weight of 22.4 l., and is therefore O_2. Half as much as this may enter into a compound, H_2O, ZnO, etc., but, logically, the formula for free oxygen must record the double weight required to fill the cube when the gas is present alone, in the free condition (see pp. 100, 102). Similarly the formula for hydrogen gas is H_2 $(2 \times 1.008 = 2.016$, the weight of 22.4 l.). *The formula of every volatile substance must thus be written so as to show the weight of the chemical unit quantity* (the molecular weight, p. 91). When the substance is not easily volatilized, this unit cannot be measured, and the simplest formula is employed.

Information Contained in Each Formula. — A formula thus contains, in condensed form, several items of information. It shows:

1. The elements making up the substance,
2. The proportion by weight of those elements,
3. The total unit weight (molecular weight) of the substance. Given the formula, we can read these facts in it.

Thus, if we are given the formula of carbon dioxide, CO_2, we consult the table of atomic weights (inside rear cover), and learn that $C = 12.005$ *parts* by weight of *carbon* and $O_2 = 2 \times 16$ *parts* by weight of *oxygen.* The proportion by weight of the

elements in this compound is, therefore, 12.005 of carbon to 32 of oxygen. The total weight (molecular weight) is $12.005 + 32 = 44.005$, and this must be the weight filling 22.4 l. (at 0° and 760 mm.).

Derivation of Formulæ from Experimental Data. — In the condensed statements presented in previous chapters, the numbers included were already multiples of the atomic weights, and the formulæ were therefore easy to make. It remains to show how the formula may be constructed from the weights obtained in an experiment.

In the quantitative experiment on the composition of cupric oxide (p. 38), the proportion found was: copper 85, oxygen 21. In the formula, the same proportion is to be expressed by means of multiples of the atomic weights. If we divide each of these numbers by the corresponding atomic weight, the quotient will be the number by which the atomic weight must be multiplied. The atomic weights are $Cu = 63.57$, $O = 16$. $85 \div 63.57 = 1.3$, and $21 \div 16 = 1.3$. The proportion of copper to oxygen in the compound, $\dfrac{85}{21}$, now becomes $\dfrac{63.57 \times 1.3}{16 \times 1.3}$.

But this proportion must be expressed in multiples of the atomic weights by *whole* numbers. Dividing above and below by 1.3, we get $\dfrac{63.57 \times 1}{16 \times 1}$.

Now the symbols stand for the atomic weights. Substituting the symbols, the proportion becomes $\dfrac{Cu \times 1}{O \times 1}$. The formula is, therefore, CuO.

Applying the same process to the case of sulphur dioxide (p. 39):

$$\frac{\text{Sulphur}}{\text{Oxygen}} = \frac{1.21}{1.21} = \frac{32.06 \times .0378}{16 \times .0756} = \frac{32.06 \times 1}{16 \times 2} = \frac{S \times 1}{O \times 2}, \text{ or } SO_2.$$

If the composition of the substance has been stated in percentages, the same device is used. Thus, the case of sodium sulphate works out as follows:

Elements.	Percentages.	At.Wt. Quotient	÷	Formula.
·Sodium . . .	32.43	23 × 1.41	0.705	Na × 2
Sulphur . . .	22.55	32 × 0.705	0.705	S
Oxygen	45.02	16 × 2.814	0.705	O × 4

The formula is, therefore, Na_2SO_4.

Formulæ obtained by this arithmetical method are known as **empirical formulæ.** They give us the correct atomic proportions of the constituent elements, expressed in the lowest possible whole number ratios. In many cases, however, it is necessary to multiply the empirical formula of a substance throughout by 2, or 3, or some other whole number greater than 1, in order to arrive at the true **molecular formula.** Some examples will be discussed in a later section (p. 118).

Equations. — The condensed statements of chemical changes which we have been using can now be simplified by using the *formulæ* in place of the names of the substances (pp. 13-14). Thus

$$C + O_2 \rightarrow CO_2.$$
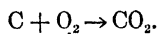
This is to be read: 12.005 parts (or 1 atomic weight) of carbon, *acting chemically with* 2×16 parts (or 2 atomic weights) of oxygen, *give* 44.005 parts of carbon dioxide. We may also read it thus: 1 atom of carbon with 1 molecule of oxygen gives 1 molecule of carbon dioxide.

In making an equation there are **four stages or steps:**

1. Find out by experiment what the substances used and produced are.

2. Learn the molecular formula of each substance.

3. Set down the molecular formulæ in the form of a skeleton equation. Place the formulæ of the *initial substances* on the *left,* and those of the products on the right.

4. Adjust, or *balance* the equation.

For example:

(1) When hydrogen and oxygen combine, water is **formed.**

(2) The molecular formulæ are H_2, O_2, and H_2O.

(3) Skeleton equation: $H_2 + O_2 \rightarrow H_2O$.

(4) In accordance with the law of conservation of mass, the numbers of atomic weights (or atoms) of each element must be the same after the action as before it. Now the skeleton equation shows two atomic weights of oxygen before, and, thus far only one after the action, whereas there ought to be two there also. With O_2 (2 × 16 parts) we have enough oxygen to give $2H_2O$, which contains 2 × 16 parts of oxygen. But this will require us to take $2H_2$ to "balance" the equation. The final equation is, therefore:

Balanced Equation: $2H_2 + O_2 \rightarrow 2H_2O$.

Observe, we could not adjust the difficulty by writing $H_2 + O \rightarrow H_2O$, because each substance must be represented by its *molecular* formula, which stands for the weight of the substance in the standard volume of 22.4 liters, or one chemical unit weight, and in the case of oxygen this is O_2 (= 32 g.). Putting this in terms of atoms and molecules, each formula must represent 1 molecule, and the molecules of oxygen contain 2 atoms. Now we could not take less than one oxygen molecule. But we *could take more than one molecule* of hydrogen, so we took 2 molecules of this substance.

The coefficients in front of formulæ multiply the *whole* formula. $2H_2O$ is equivalent to $2(H_2O)$, or two whole molecules of water.

Balancing Equations. — Learning to balance equations correctly comes only by practice. Take, again, the case of iron rusting. The substances are iron (Fe), oxygen (O_2) and ferric oxide (Fe_2O_3). The skeleton equation is

$$Fe + O_2 \rightarrow Fe_2O_3.$$
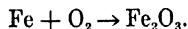
We are not permitted to alter these formulæ themselves, but we may put coefficients in front of any of them to make the number of atomic weights alike on both sides. A good rule is *to pick out the largest formula and reason back from that.* Here, this is Fe_2O_3. To get oxygen atoms in *threes,* we must clearly take $3O_2$ (= 60). That will give us $2Fe_2O_3$. This, in turn, will require 4Fe:

*Balanced:* $4Fe + 3O_2 \rightarrow 2Fe_2O_3$.
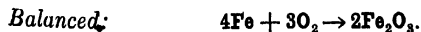
The student should endeavor to obtain all possible experience in writing and balancing equations by turning back to the condensed statements of chemical changes in earlier chapters, and converting them into the above form. For his additional guidance, a few illustrative examples are given in the next section.

Equations for Actions Already Studied. — In the *preparation of oxygen* (p. 19) we used mercuric oxide and got mercury and oxygen:

Skeleton: $HgO \rightarrow Hg + O_2$.
Balanced: $2HgO \rightarrow 2Hg + O_2$.

Potassium chlorate has a composition shown by the formula $KClO_3$. It gives (p. 31) potassium chloride (KCl) and oxygen (O_2).

Skeleton: $KClO_3 \rightarrow KCl + O_2$.
Balanced: $2KClO_3 \rightarrow 2KCl + 3O_2$.
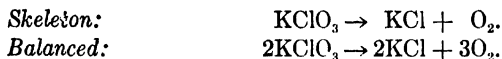
The variety of chemical change, where one substance gives two (or more) substances, *decomposition* (p. 19), is readily recognized in these equations.

Substances, like the manganese dioxide (catalytic agent) used here, and the water so often employed as a solvent, **when they undergo no chemical change, are omitted from the equation.**

When the water takes part in the action, however, it must, of course, be included. Thus sodium peroxide (Na_2O_2) and water (H_2O) interact (p. 32) to give sodium hydroxide and oxygen:

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2.$$
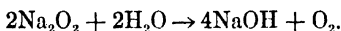
The preparation of hydrogen (p. 59) from sodium (Na) and water gives sodium hydroxide (NaOH) and hydrogen (H_2):

$$2Na + 2H_2O \rightarrow 2NaOH + H_2.$$
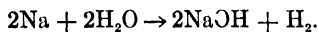
When steam is passed over iron (p. 60), we get hydrogen and magnetic oxide of iron (Fe_3O_4):

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$
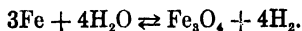
The liberation of hydrogen by the action of zinc (Zn) upon sulphuric acid (H_2SO_4), where the products (p. 62) are hydrogen. and zinc sulphate, is shown thus:

$$Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4.$$
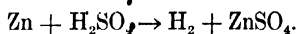
Again, iron and hydrochloric acid (HCl) give hydrogen and ferrous chloride ($FeCl_2$):

$$Fe + 2HCl \rightarrow H_2 + FeCl_2.$$
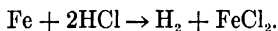
In the last two equations the variety of chemical changes called *displacement* (p. 59), where one elementary substance displaces another from a compound, is well illustrated.

The equation for the *formation of water* by union of hydrogen and oxygen,

$$2H_2 + O_2 \rightarrow 2H_2O,$$
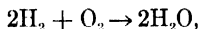
has already (p. 113) been discussed. The *reduction* of an oxide, such as magnetic oxide of iron or cupric oxide, by hydrogen (p. 70), gives the metal and water:

$$Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O.$$
$$CuO + H_2 \rightarrow Cu + H_2O.$$
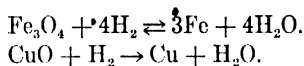
Upon examining these equations for reductions, we perceive that they are illustrations of displacement also.

Reversible actions (p. 85), like the decomposition of water by heating, and the recombination of the elements on cooling (p. 82), are shown by using two arrows:

$$2H_2O \rightleftarrows 2H_2 + O_2.$$
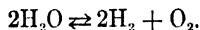
The equation may be read from either end. The decomposition and formation of hydrates (p. 84) are also reversible actions. In the case of zinc sulphate, the equation is

$$ZnSO_4 + 7H_2O \rightleftarrows ZnSO_4,7H_2O.$$
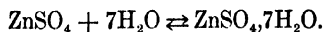
Reaction Formulæ. — In the foregoing formula for the hydrate of zinc sulphate, it will be seen that we do *not* add together all the atoms of oxygen, and write $ZnH_{14}SO_{11}$. The latter would show the composition of the substance correctly, but

it would show *nothing more.* Now chemists find it convenient,
frequently, to alter the formula so that it shall indicate also *some
important* chemical property or *reaction* of the substance. Hence
the formula $ZnSO_4,7H_2O$, which indicates at a glance the rela-
tionship of the substance to zinc sulphate $(ZnSO_4)$. The hydrate
is *made from* zinc sulphate by adding water, and is easily *decom-
posed into* these two substances again. The reaction formula
hints at this familiar *reaction.* Note, however, that the comma
(,) does *not* indicate a *mixture* of the materials, such as $ZnSO_4$
and H_2O, but a single substance composed of both. The plus
(+) sign is used between the formulæ of different, uncombined
substances in a mixture.

In accordance with this plan, washing soda, hydrate of sodium
carbonate (p. 83), is written $Na_2CO_3,10H_2O$, and bluestone (p.
84), hydrate of cupric sulphate, $CuSO_4,5H_2O$.

Significance and Use of Molecular Formulæ. — In this chap-
ter we have already emphasized the fact that the formula must
represent a molecular weight of the substance, as well as its
composition. The total weight, for which the symbols in a
formula stand, must be equal to the weight of the substance
occupying the gram-molecular volume. In other words, the
formula-weight must represent one cube-full (Fig. 43, p. 90) of
the substance. This is true, as we have seen, of the formulæ
H_2O and HCl (see p. 93).

In the cases of tin oxide (SnO_2) and ferric oxide (Fe_2O_3), we
have substances which cannot be converted into vapor or dis-
solved (see p. 153), so that their molecular weights are unknown.
In such cases, we use the simplest formula that will show the
correct proportions.

The student should return now to the tables on pp. 93 and
95, and deduce for himself the formulæ of the various elements
and compounds there included.

Molecular Formulæ of Elementary Substances. — Some fur-
ther explanation may be required, to the end that the reader may
be reconciled to accepting the formulæ Cl_2, O_2, and so forth,
deduced from the table on p. 93. In the first place, he should

note how these formulæ arose. If we accept Avogadro's law, and the inference from it to the effect that the weights of equal volumes of gases are in the same ratio as the weights of their individual molecules, then we cannot escape the conclusion to which measuring the relative densities of free chlorine and hydrogen chloride, for example, leads. The ratio of their densities is 70.92 : 36.46. That is to say, the relative weights of a molecule of chlorine and a molecule of hydrogen chloride stand in this ratio. The molecule of chlorine is nearly twice as heavy as the molecule of the compound, *and there cannot therefore be a whole* **molecule of** *chlorine in a molecule of hydrogen chloride.* In fact, we perceive at once that the molecule of hydrogen chloride must contain only half a molecule of chlorine (35.46), together with half a molecule of hydrogen (1). In other words, if the molecule of free chlorine were to be taken as the atom of the element, then the molecule of hydrogen chloride would contain only half an atom of chlorine, which would be contrary to our definition to take as atoms quantities which are not divided. So we choose the other horn of the dilemma, and say that the specimen of chlorine in the molecule of hydrogen chloride is a whole atom and that therefore the amount of chlorine in the molecule of free chlorine is two atoms, and its formula Cl_2. Similarly, the weight of hydrogen in the molecule of hydrogen chloride is 1.008, while that of the molecule of hydrogen is 2.016, so that there are two atoms in the molecule of free hydrogen and its formula is H_2. Reasoning in like manner from the molecular weights of oxygen (32) and water (18) we reach the conclusion (compare p. 100) that the molecule of oxygen is diatomic (O_2).

The simple fact that hydrogen and oxygen, when mixed, do not combine (p. 68) may assist in reconciling us to the diatomic nature of their molecules. Some part of the mixture has to be heated strongly to start the interaction. Now the molecular formulæ, H_2 and O_2, suggest that each gas is really in combination already (with itself), and they therefore explain to some extent the indifference of the gases towards one another. If the molecules were free atoms, they could not encounter one another continually as they move about, and yet escape combination as we observe that they do. We may imagine that the primary

effect of heating is to decompose some of the molecules, and liberate hydrogen and oxygen in the atomic condition, and that the combination of these atoms starts the explosion of the whole mass.

In the case of hydrogen, the diatomic nature of the molecules has been demonstrated by an entirely different method by Langmuir. It has long been known that the conductivity of hydrogen for heat is greater than that of any other elementary gas. Thus, a wire raised to a white heat in air by means of an electric current, cannot be kept at a red heat, even, by the same current in hydrogen. In air, heat from the hot wire is used up solely in accelerating the motion of the molecules of the gas. Langmuir has shown, however, that in hydrogen, additional heat is consumed in causing decomposition of many of the diatomic molecules into single atoms:

$$H_2 \rightleftarrows 2H.$$
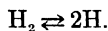
He has measured the percentage of molecules dissociated (at 760 mm.), and found that it varies from 0.33 per cent at 2000° to 13 per cent at 3000° and 34 per cent at 3500°. When the temperature falls, the atoms re-combine to diatomic molecules.

Molecular Formulæ of Compounds. — If the molecular formulæ deduced for the compounds in the table on p. 95 be now examined it will be observed that several of these also are not in their simplest terms. Thus, the formula of acetylene is C_2H_2. The formula CH would represent the composition of the substance equally well, for $12.005 : 1.008$ is the same as $24.010 : 2.016$. But the formula CH gives a total of only 13.013, while C_2H_2 shows the total weight of the molecule to be 26.026 and is in accordance therefore with *the weight of the G.M.V.*, as well as with the composition of the substance. Similarly the molecular formula of acetic acid is $C_2H_4O_2$, and not the simpler, identical proportion CH_2O. The latter is the molecular formula of a totally different substance, formaldehyde, now much used as a disinfectant. The vapor of this substance has only half the density of acetic acid vapor, and this fact, recorded in the formula, helps to remind us that the substances are different. Still

another substance of the same composition is grape sugar (dextrose), $C_6H_{12}O_6$.

Molecular formulæ like C_2H_2 and $C_2H_4O_2$ are easily interpreted in terms of the atomic hypothesis. C represents one atom of carbon and H one atom of hydrogen. But there is no reason why a molecule of acetylene should not contain two atoms of each kind. Similarly, the molecule of formaldehyde contains four atoms (CH_2O), and one of acetic acid eight atoms ($C_2H_4O_2$), and one of dextrose twenty-four atoms ($C_6H_{12}O_6$), although the relative numbers of each kind are the same. Indeed this hypothesis helps to clear the matter up, for chemists go so far as to account for the chemical behavior of the substances by an imagined geometrical arrangement of the atoms in their molecules, and these three kinds of molecules are supposed to differ in structure as well as in the number of atoms they contain.
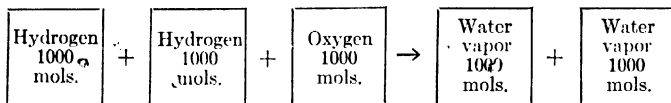
Applications: Interactions Between Gases. — According to Avogadro's law, if we filled a succession of vessels of equal dimensions with different gases, and could arrest the motion of the particles and observe their disposition, we should find that the average distance from particle to particle would be the same in all cases. This would be true whether our vessels were filled with single gases, with homogeneous mixtures, or with gases in layers. Such being the case, if any chemical change is brought about in the mass which results in a multiplication of the molecules, it is evident that the volume will have to increase in order that the spacing may remain the same as before. If any chemical action results in a diminution of the number of molecules, then a shrinkage must take place in order that the spacing may be preserved as before. Thus, in a mixture of hydrogen and oxygen, according to our hypothesis, when the interaction occurs, the following change takes place between neighboring molecules:

$$HH + OO + HH \text{ becomes } HOH + HOH.$$
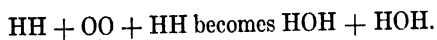
Since the oxygen molecules, which form a third of the whole, disappear into the molecules of hydrogen, the tendency to preserve spacing results in a diminution of the volume by one-third (p. 72). Thus Gay-Lussac's law would have followed as a nat-

ural inference from Avogadro's law, if the former, being more obvious, had not been discovered first.

If each of the following squares represents a small volume containing 1000 molecules of gas, then 2000 molecules of hydrogen and 1000 molecules of oxygen give 2000 molecules of water vapor. We may note again, in passing, that, since each molecule of water must contain at least one atom of oxygen, at least 2000 atoms of oxygen were required, and must have been furnished by the 1000 molecules of oxygen. Each of these molecules must therefore have split into two atoms.

Hydrogen 1000 mols.	$+$	Hydrogen 1000 mols.	$+$	Oxygen 1000 mols.	$\rightarrow$	Water vapor 1000 mols.	$+$	Water vapor 1000 mols.

This method of looking upon chemical interactions between gases gives us the nearest sight which we can have of the behavior of the molecules themselves. We cannot perceive the individual molecules, but, in consequence of the spatial arrangement which they observe, the change in the whole volume of a large aggregate of molecules enables us to draw conclusions at once in regard to the behavior of the single molecules in detail.

Applications: Molecular Equations. — To utilize the foregoing considerations, chemists **always employ in their equations the molecular formulæ** for the gases and the easily vaporized substances concerned. Thus, if we used the equation:

$$2H \quad + \quad O \quad \rightarrow \quad H_2O$$

WEIGHTS: 2×1.008 16   18.016
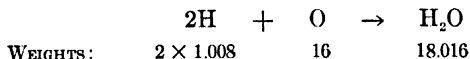
the information it contained would be exhausted when we had placed below the symbols the weights for which they stood. But the molecular equation is much more instructive. The following shows **the interpretations to which the molecular equation is subject:**

$$2H_2 \quad + \quad O_2 \quad \rightarrow \quad 2H_2O$$

WEIGHTS: 2×2.016 g.   32 g. 2×18.016 ($= 36.032$) g.
VOLUMES: 2×22.4 l.   22.4 l. 2×22.4 l.
MOLECULES: 2   1   2
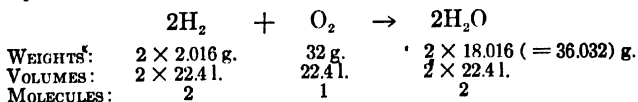
The weights, although doubled, show the same proportions, so that questions of weight are answered as easily as before. These weights, however, being molecular weights, or multiples thereof, can be translated at 'once into *volumes*, and **questions about volumes can also be answered.** Finally, **the relative numbers of each kind of molecules can be read from this equation,** for the coefficients in' front of the formulæ represent these numbers. Where no coefficient is written, 1 is to be understood.*

Applications: To Cases of Dissociation. — Certain gases or vapors yield abnormally small values for their densities, and therefore for their molecular weights derived by reducing these density values to standard conditions (22.4 l. at 0° and 760 mm.), when examined at higher temperatures. This indicates that the molecules have become lighter, and can only mean that decomposition has taken place in consequence of the heating. Behavior of this kind is shown both by compounds and by simple substances.

For example, phosphorus pentachloride PCl_5, although a solid, can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be $31 + 177.3 = 208.3$. The density actually observed at 300° and 760 mm. pressure gives by calculation a molecular weight not much more than half this value. The direct inference from this is that the molecules have not much more than half the (average) weight that we expected; or, in other words, are almost twice as numerous as we expected. The explanation is found when we examine the nature of the vapor more closely. We find that it actually contains very little phosphorus pentachloride, but is almost entirely a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The low value of the density thus tells us that dissociation has taken place. From the value of the density at various temperatures and pressures, we may even calculate the proportion of the whole material

* The application of these properties of molecular equations is illustrated in Chap. XIII (pp. 188-191). If desired, these applications may be taken up after the next section.

which is dissociated under any given conditions. At 300° it is
97 per cent; at 250°, 80 per cent; and at 200°, 48.5 per cent
(under a pressure of 760 mm.). Thus, when the temperature is
lowered, progressive recombination takes place and the propor-
tion dissociated becomes less. Finally the vapor condenses and
yields the original solid.

Again, sulphur boils at 445°, but can be vaporized at a tem-
perature as low as 193°, under very low pressure. At this tem-
perature the density of the vapor gives the molecular weight 256
($= 8 \times 32$) and the molecular formula S_8. At 800°, however,
the molecular weight indicated by the density is only one-fourth
as great, and the molecular formula is accordingly S_2. At 1700°
the molecular formula is still S_2, so that this represents the limit
of dissociation: $S_8 \rightleftarrows 4S_2$. When the vapor is cooled, the molec-
ular weight derived from density determinations increases once
more and at 193° recovers completely the greater value. Similar
observations show that phosphorus vapor at 313° is all P_4, but
at 1700° and 760 mm. one-half of the molecules are P_2. Iodine
vapor, up to 700°, is all I_2. Beyond this temperature the density
diminishes abnormally, and when 1700° is reached the vapor is
all I. Thus the molecules are diatomic at low temperatures and
monatomic at high ones. The densities of oxygen, hydrogen, and
chlorine vary quite normally, in accordance with the gas laws,
on heating to 1700°, so that their diatomic molecules exist from
temperatures far below 0° up to 1700°, and are evidently very
stable. For observations on hydrogen above 1700°, however,
see p. 118.

CALCULATIONS

As we have seen (p. 109), the formula represents the composi-
tion of a substance, using the atomic weights as the units. We
have learned how the formula is calculated from measurements
made in an experiment (p. 111). We may now take up some of
the ways of using the information contained in a formula.

Composition from the Formula. Formula-Weight. —
To learn the composition of a substance, such as potassium
chlorate, $KClO_3$, from its formula, we look up the values of the
atomic weights (inside rear cover). We find $K = 39.1$ parts of

potassium, $Cl = 35.46$ parts of chlorine, and $O_3 = 3 \times 16.00$ or 48 parts of oxygen. The proportions, in order, are therefore: 39.1 : 35.46 : 48. •

What is the proportion of óxygen to potassium and chlorine, together?. It is 48 : 39.1 + 35.46, or 48 : 74.56, or 1 : 1.55.

We require a name for the sum of the weights of the constituents indicated in the formula. This is called the **formula-weight**. Thus, for potassium chlorate, it is $39.1 + 35.46 + 48$, or 122.56.

To Find the Percentage Composition. — In potassium chlorate the proportions are 39.1 of potassium, 35.46 of chlorine, and 48 of oxygen in a total of 122.56. In one hundred parts, the potassium is $\dfrac{39.1}{122.56} \times 100$, or 31.9%; the chlorine $\dfrac{35.46}{122.56} \times 100$, or 28.9%; and the oxygen $\dfrac{48}{122.56} \times 100$, or 39.1%.

Stated in terms of the rule of proportion, we have, for the potassium, $122.56 : 39.1 :: 100 : x$, where x is the percentage of potassium.

Calculations by Use of Equations. — We frequently wish to know what weight of a product can be obtained from a given weight of the necessary materials. For example, what weight of ferrous sulphide can be made with 100 g. of iron? It is understood, of course, that the necessary sulphur is available.

To avoid the blunders which are easily made, observe strictly the following rules:

1. **Write down the equation:**

$$Fe + S \rightarrow FeS.$$
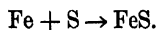
2. **Place under each formula the weight it represents:**

$$Fe + S \rightarrow FeS$$
$$55.84 \quad 32.06 \quad 87.90$$

3. **Read this expanded equation.** In this case it reads: 55.84 parts of iron combine with 32.06 parts of sulphur to give 87.90 parts of ferrous sulphide.

4. Re-read the original problem: "Whaṫ weight of ferrous sulphide can be made with 100 g. of iron?" Having done this, place the amount given in the problem (100 g. of iron) under the formula of the substance in question. Then notice what the problem asks ("what weight of ferrous sulphide") and place an x under the formula of that substance:

$$Fe \;+\; S \;\rightarrow\; FeS$$
$$55.84 \qquad 32.06 \qquad 87.90$$
$$100\ g. \qquad\qquad\qquad x$$
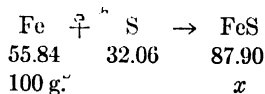
5. **Read the problem as now tabulated:** 55.84 g. of iron give 87.90 g. of ferrous sulphide, therefore 100 g. of iron will give x g. of ferrous sulphide.

6. **State the proportion in this order** (or, see below).

$$55.84 : 87.90 :: 100 : x \quad (\,= 157.4\ g).$$

If the tabulation in rule 4 has been prepared correctly, this final statement as a proportion is purely mechanical. It will be noted that only two of the three quantities given in the expanded equation were actually used.

6a. **Alternative Method.** At the sixth step, we may also say: If 55.84 g. of iron give 87.90 g. of ferrous sulphide, 1 g. of iron will give $\dfrac{87.90}{55.84}$ g. ($= 1.574$ g.) of ferrous sulphide. Then, if 1 g. of iron gives 1.574 g. of ferrous sulphide, the 100 g. of iron will give 100×1.574 g. ($= 157.4$ g.) of ferrous sulphide.

Warnings. — In solving the exercises at the end of the chapter, beware of *three kinds of mistakes* commonly made by beginners.

1. Conquer a tendency to say that the symbols Fe and S stand for " 1 part " of iron or of sulphur. They stand for 1 *chemical unit,* or atomic weight, or atom, in each case, — that is to say, for 55.84 " parts " and 32.06 " parts," respectively.
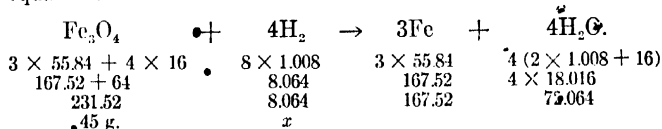
2. Follow the rules laid down above. When one has once *become familiar* with the art of solving such problems, running through the rules takes only a few seconds. The chemist does it almost unconsciously. The beginner *always* thinks he can ignore

these rules, and he fails in consequence. Writing the equation in the expanded form, and then reading the problem into it are absolutely essential steps.

3. Do not read the original problem carelessly and make the equation *backwards*, that is, with the sides reversed. If there seems to be confusion somewhere, where the last steps are reached, this hint will probably show the cause of the difficulty.

Another Example. — What weight of hydrogen is required to reduce 45 g. of magnetic oxide of iron to metallic iron?

Following the rules, as before, we reach the expanded equation:

$$Fe_3O_4 \quad + \quad 4H_2 \quad \rightarrow \quad 3Fe \quad + \quad 4H_2O.$$

$3 \times 55.84 + 4 \times 16$	8×1.008	3×55.84	$4 \ (2 \times 1.008 + 16)$
167.52 + 64	8.064	167.52	4×18.016
231.52	8.064	167.52	72.064
45 g.	x		

Observe that the atomic weights are multiplied by the sub-numbers, so that, for example, $Fe_3 = 3 \times 55.84$. Observe also that the formula weights are multiplied by the coefficients, when such occur, in front of the formula, so that, for example, $4H_2O = 4 \times 18.016$.

The proportion $231.52 : 8.064 :: 45 : x \ (= 1.57)$ supplies the answer, 1.57 grams of hydrogen.

Using the **alternative plan** (p. 124): If 231.52 g. of magnetic oxide are reduced by 8.064 g. of hydrogen, 1 g. will be reduced by $\dfrac{8.064}{231.52}$ g. $(= 0.035$ g.$)$ of hydrogen. Hence, if 1 g. of magnetic oxide is reduced by 0.035 g. of hydrogen, 45 g. will be reduced by 45×0.035 g. $(= 1.57$ g.$)$ of hydrogen.

Exercises. — 1. From the data on p. 13 and the atomic weights, calculate the formula of lead oxide. Construct also the equations for the decomposition of potassium nitrate (p. 30), and for the combination of phosphorus and oxygen (p. 36).

2. When 1 g. of sodium burns in oxygen, it produces 1.7 g. of the oxide. What is the formula of the latter and the equation?

3. If 26 g. of mercurous oxide are required to give, by heating, 1 g. of oxygen, what is the formula of the substance?

4. What are the formulæ of the substances possessing the following percentage compositions?

I	II	III
Magnesium, 25.57	Sodium, 32.43	Potassium, 26.585
Chlorine, 74.43	Sulphur, 22.55	Chromium, 35.390
	Oxygen, 45.02	Oxygen, 38.025

5. What are the percentage compositions of substances possessing the following formulæ: Mn_3O_4, KBr, $FeSO_4$?

6. What weight of mercury is obtained from 120 g. of mercuric oxide HgO?

7. What weight of mercuric oxide will furnish 20 g. of oxygen?

8. What weight of Fe_2O_3 may be obtained from 10 g. of oxygen?

9. How much silver is contained in 100 g. of an impure specimen of silver chloride $AgCl$ which is 33 per cent sand?

10. What are the percentage compositions of cerium sulphate $Ce(SO_4)_2$, phosphorus pentachloride PCl_5, and ammonium chloride NH_4Cl?

11. What weight of hydrogen is required to reduce 100 g. of ferric chloride $FeCl_3$ to ferrous chloride $FeCl_2$?

12. Gypsum is a hydrate of calcium sulphate ($CaSO_4$). If 6 g. of gypsum, when heated, lose 1.256 g. of water, what is the formula of the hydrate?

CHAPTER X

VALENCE

Equivalence and Valence. — If the condensed statements
showing displacement of hydrogen by a metal be now rewritten
in the form of equations, a peculiarity will be observed which
we have thus far omitted to note. When sodium and calcium
(p. 59) act upon water, each atomic weight (or atom) of the
former displaces one atomic weight of hydrogen, but each atomic
weight of the latter displaces twice as much hydrogen. Again,
one atom of zinc (p. 62) displaces two atoms of hydrogen, but
one atom of aluminium displaces three. Assuming, for simplicity,
that we allow these metals all to act upon dilute hydrochloric
acid, the equations are:

$$2Na + 2HCl \rightarrow 2NaCl + H_2.$$
$$Ca + 2HCl \rightarrow CaCl_2 + H_2.$$
$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$
$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2.$$
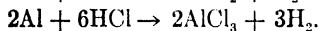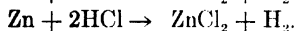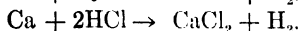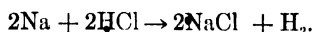
Interpreting this, we perceive that each atom of aluminium,
for example, displaces 3 atoms of hydrogen, *because it is able to
combine with 3 atoms of chlorine,* and so incidentally liberates
the hydrogen formerly united with these 3 atoms of chlorine.
Each atom of sodium, however, can unite with only 1 atom of
chlorine, and so releases only 1 atom of hydrogen. Now this is
not a rule confined to these reactions, but represents a general
chemical property of the atomic weight of each element, and a
property which we shall find most useful.

The atom of aluminium releases 3 atoms of hydrogen because
it can take the place of 3 atoms of hydrogen in chemical com-
bination (and hold 3 atoms of chlorine). The atomic weight
of aluminium is said to be *equivalent to* (equal in chemical value
to) 3 atomic weights of hydrogen (compare p. 64). Since it

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combines with 3 atomic weights of chlorine, it is also considered to be equi-valent to 3 atomic weights of this element.
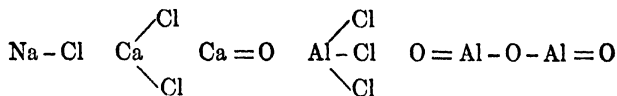
The *chemical property* referred to is called **valence**. The valence of an atomic weight of hydrogen or of chlorine is the unit. An atomic weight of sodium is said to be **univalent**, one of calcium **bivalent**, one of aluminium **trivalent**. The formula H_2O shows the atomic weight of oxygen to be bivalent, because it unites with two atomic weights of hydrogen. Apparently, the atomic weight (or atom) of each element has a fixed capacity for combining with not more than a certain number of atomic weights (or atoms) of other elements.

Marking the Valence. — Until we have become familiar with the valence of each element, it is advisable to mark the valences in a special way: Na^I, Ca^{II}, Al^{III}, O^{II}, Zn^{II}, Cl^I.

As we should expect, a bivalent atom can combine with two univalent atoms, *or with one bivalent atom,* and so forth. Thus we have the compounds of oxygen: $Na_2^I O^{II}$, $Ca^{II}O^{II}$, $Al_2^{III}O_3^{II}$, $Zn^{II}O^{II}$, $Cl_2^I O^{II}$.

The rule is that the quantities of two elements which combine must have equal total combining capacities—*i.e.,* identical total valence. Thus, Ca^{II} has the valence two, and so does O^{II}. Again, Al_2^{III} has a total valence of 2×3 ($= 6$) and so has O_3^{II} ($3 \times 2 = 6$).

Frequently the valence is marked by means of lines, the number of lines pointing towards a symbol indicating the valence of the atom it represents:
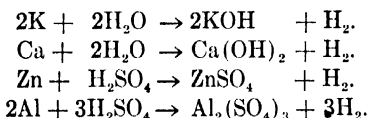
$$Na - Cl \qquad Ca\!\!\underset{\diagdown Cl}{\overset{\diagup Cl}{}} \qquad Ca = O \qquad Al\!\!\underset{\diagdown Cl}{\overset{\diagup Cl}{-Cl}} \qquad O = Al - O - Al = O$$

Definition. — The **valence of an element is a number representing the capacity of its atomic weight to combine with, or displace, atomic weights of other elements, the unit of such capacity being that of one atomic weight of hydrogen or chlorine.**

Stated more briefly, **the valence of an element is the number of atoms of hydrogen, or of chlorine, which the atom of the given element can combine with or displace.**

· **Valence of Radicals.** — What we have said applies to com-
pounds of not more than two elements — so-called **binary**
compounds. We cannot, by inspection, tell the valences in a
compound of three or more elements, like sulphuric acid H_2SO_4.
But we have seen (p. 61) that the acids behave as if composed
of two radicals: $H(Cl)$, $H_2(SO_4)$, that is, of two groups which
move as wholes in chemical reactions. Hence we can assign a
valence to a compound radical *as a whole.* Thus $(SO_4)^{II}$ is evi-
dently bivalent, as a whole, because it is united with $2H^I$.
$Na(OH)$ and $Ca(OH)_2$ show the radical **hydroxyl** (OH), present
in hydroxides or bases (p. 83), to be univalent.

The re-writing of a few condensed statements of chemical
changes in which these radicals are concerned (pp. 59, 62) will
make the above statements more obvious to the student.

$$2K + 2H_2O \rightarrow 2KOH + H_2.$$
$$Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2.$$
$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2.$$
$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2.$$

It is to preserve the identity of the radicals, and to make them
easily recognizable, that we write them in brackets and place the
coefficient outside, as $Ca(OH)_2$ and $Al_2(SO_4)_3$, instead of using
the forms CaO_2H_2, $Al_2S_3O_{12}$, and so forth. In fact, substances
which commonly interact as if the radicals were single elements,
we regard as binary compounds.

In writing formulæ of inorganic compounds we usually place
the positive radical (p. 61) in front and the negative radical
after it.

Use in Making Formulæ and Equations. — The chief use of
the conception of valence is the very practical one of enabling
us to write formulæ. In making equations we constantly need to
know whether the chloride of an element, say magnesium, is
$MgCl$, or $MgCl_2$, or $MgCl_3$, or $MgCl_4$, etc., and whether its sul-
phate is $MgSO_4$, or Mg_2SO_4, or some other combination of the
symbols. To answer questions like this it is not necessary to
know the formula of every compound of each element; the ap-
parent disorder of these numbers can be reduced to rule, and the

reader should endeavor thoroughly to master the rule before
going farther.

Suppose, for example, that we burn a piece of magnesium
ribbon in chlorine, and get magnesium chloride. What is its
formula? Up to this point, we should simply have looked for
it in a book. And if, subsequently, we had required the formulæ
of the oxide and sulphate of-magnesium, we should have looked
these up separately also.

But now, all we have to do is to *find out the valence of mag-
nesium.* Knowing already the valences of Cl^I and O^{II} and
$(SO_4)^{II}$, we have then all the information we require for making
the needed formulæ. Suppose we find that the atomic weight
of magnesium is bivalent, Mg^{II} (see next section). Making the
total valences of each half of the compound alike, we get the
formulæ:

$$Mg^{II}Cl_2{}^I, \ Mg^{II}O^{II}, \ Mg^{II}(SO_4)^{II}.$$
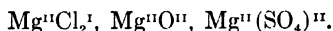
When we know the valences of the elements and radicals, we can
make the formula of any required compound.

*The reader must therefore make a special effort always to
learn the valences of each element and radical, and always to
use them in making formulæ.*

The reader must also always *check every formula he writes
from memory,* to make sure that it is correct. Thus, if he thinks
the formula of zinc nitrate is $ZnNO_3$, he must count the valences.
$Zn^{II}(NO_3)^I$. Evidently, the *correct* formula is $Zn(NO_3)_2$.

How to Learn the Valence of an Element. — To find out
the valence of an element, we must obtain the formula of one sim-
ple compound of the element, containing another element of
known valence. Thus, what is the valence of carbon? Its oxide
is CO_2. The total valence of the two oxygen atoms here is
$2 \times 2 = 4$. Carbon C^{IV} is therefore *quadrivalent.* Hence its
chloride must be $C^{IV}Cl_4{}^I$ (carbon tetrachloride), and its compound
with hydrogen $C^{IV}H_4{}^I$ (methane, composing a large part of nat-
ural gas). When carbon combines with a trivalent element,
equi-valent amounts of each element must be used, as in
$Al_4{}^{III}C_3{}^{IV}$ (aluminium carbide), where $Al_4{}^{III}$ and $C_3{}^{IV}$ contain
3×4, or 12 units of valence each.

. Again, when we know the formula of sodium iodide to be Na^{I}I, or that of hydrogen iodide to be H^{I}I, we infer that iodine is· *univalent.* The formula of silica (sand) SiO$_2$^{II} shows silicon to be *quadrivalent,* and indicates that the chloride must be SiCl$_4$. Similarly the formula of calcium carbonate Ca^{II}CO$_3$ shows that the radical CO$_3$,· which is common to all carbonates, must be *bivalent.*

The chemist does not memorize the valences themselves; he recovers the valence of an element or radical, when needed, by recalling the formula of a substance containing this element or radical in combination with a more familiar element or radical, such as Cl^{I} or H^{I}.

In subsequent chapters (pp. 356, 730) we shall find that the valence of an element is not a purely fortuitous number, since we can formulate rules by which the valence of any given element may be deduced. We shall thus obtain more definite ideas regarding the *significance* of valence and the mechanism of chemical combination in general. The foundations for these ideas, however, must first be developed in intervening chapters.

Elements with More than One Valence. --- The rule of valence is not quite so simple as it has thus far appeared to be. A number of the elements exhibit more than one valence. In other words, the capacity of an atomic weight of such an element may have two (or even more) values, according to the circumstances under which it is combining with other elements.

Thus, phosphorus is usually quinquivalent, and gives compounds like PCl$_5$, P$_2$O$_5$, PBr$_5$. But it can also form compounds in which it is trivalent, like PH$_3$, PCl$_3$. Similarly, iron forms two complete series of compounds:

Bivalent: FeCl$_2$,   FeO,   Fe(OH)$_2$,   FeSO$_4$.
Trivalent: FeCl$_3$,   Fe$_2$O$_3$,   Fe(OH)$_3$,   Fe$_2$(SO$_4$)$_3$.

Even the halogens, although uniformly univalent in their compounds with hydrogen and other positive radicals, show oxygen compounds of higher valence, such as chlorine dioxide ClO$_2$, iodine pentoxide I$_2$O$_5$. When an element does give more than one

series of compounds, however, we always make a strong point of this fact, so that it may not be overlooked.

The fact that an element, under different conditions, may exhibit different valences need not confuse the student as to the validity of the general conception of valence. Although it is possible for an atom of phosphorus to combine with five atoms of chlorine, this does not make it necessary that the maximum combining capacity should be exercised in all of the compounds of phosphorus. To use an analogy, the circumstance of a man having five dollars in his pocket which he is at liberty to spend does not compel him to squander the whole five dollars; he may under certain circumstances decide to save two. When an element exhibits less than its maximum valence in any given compound, it is said to be *unsaturated*. Just as the man in our illustration above still has two dollars to spend if a change of circumstances induces him to change his mind, so phosphorus in phosphorus trichloride may become *saturated* by the combination of each atom of phosphorus in the compound with two additional atoms of chlorine to form phosphorus pentachloride. The conditions necessary for this combination to take place have already been discussed (p. 121).

No simple rule, for telling, in advance, which valence will be used in a given action, can be stated. But the radicals Fe^{II} and Fe^{III}, for example, have different properties, and are easily recognized in practice.

As a rule, an element passes from one form of combination to another without change of valence. But compounds of elements like tin or manganese can undergo changes in the course of which the valence alters. Such changes will be discussed fully when we encounter examples of them in later chapters.

Exceptional Compounds. — A few compounds will be met with in which an element shows an exceptional valence. Thus, nitrogen gives two series of compounds of N^{III} and N^V. But there are three oxides, N_2O, NO, and NO_2, in which the valence of nitrogen seems to be one, two, and four, respectively. However, these are single compounds, not belonging to any series, and are

the only compounds of nitrogen showing any of those three valences.

Again, FeO and Fe_2O_3 belong to the two regular series of compounds of iron. But there is the magnetic oxide, Fe_3O_4, where the valence of iron appears not to be a whole number, but 8/3 or $2\frac{2}{3}$. In this case the chemist makes the valence regular by supposing the magnetic oxide to be a compound of the other two oxides, and writing its formula FeO,Fe_2O_3.

Nomenclature. — The names of compounds containing only two elements (the true binary compounds) end in ide. Such are the oxides, as ferric oxide Fe_2O_3; the carbides, as aluminium carbide Al_4C_3; the chlorides, as sodium chloride $NaCl$; the sulphides, as ferrous sulphide FeS, etc.

When an element forms two (or more) compounds with another element, they are frequently distinguished thus: carbon dioxide CO_2, carbon monoxide CO; phosphorus pentoxide P_2O_5, phosphorus trioxide P_2O_3.

To distinguish two compounds of the same elements, another plan is also used: ferrous chloride $FeCl_2$, ferric chloride $FeCl_3$; mercurous oxide Hg_2O, mercuric oxide HgO. The suffix ous indicates that the metal is combined with the smaller proportion of the negative element, and ic that it is combined with the larger proportion.

The tendency — although not a universal rule — is to use the latter plan with compounds containing a metal and the former with compounds containing only non-metals.

Equivalent Weights. — In the foregoing discussion of valence, we have more than once used the word "equivalent." For example (p. 127), it was stated that the atomic weight of aluminium is equivalent to three atomic weights of hydrogen, because it displaces them, and to three atomic weights of chlorine, because it combines with that number:

	2Al	+	6HCl	→	2AlCl₃	+	3H₂
Weights:	54.0		218.808		266.76		6.048
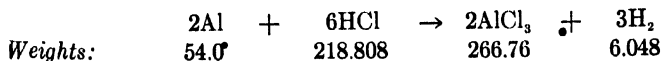
Now chemists often view this from the other direction, and say that 1.008 g. of hydrogen (one atomic weight) are displaced by 9.0 g. of aluminium (one-third of the atomic weight) and that 35.46 g. of chlorine combine with just this same quantity, 9.0 g. of aluminium. When taking this view, they refer to the **weight of an element displacing one atomic weight of hydrogen, or combining with one atomic weight of chlorine** (or of any other univalent element) as the **equivalent weight of that element.** The equivalent weight of aluminium is, therefore 9.0 and that of calcium Ca^{11} 20 (one-half the atomic weight) and that of sodium Na^{1} 23 (the atomic weight).

It will be seen that the equivalent weight can always be found by a quantitative experiment (see p. 64). It is also evident that it is equal to the atomic weight divided by the valence. It is likewise clear that the equivalent weight of an element, multiplied by the valence of that element, is equal to the atomic weight. The conception of equivalent weights finds important application later in several connections in chemistry (see Normal Solutions and Faraday's Law).

Finding the Atomic Weight of a New Element. — By way of reviewing the fundamental principles explained in this and preceding chapters, let us apply them to the imaginary case of a newly discovered metallic element. The bromide of the element is found to be easy of preparation and to be volatile. The bromide contains 30 per cent of the element (and therefore 70 per cent of bromine), and its vapor density referred to air is 11.8. The analysis can always be made much more accurately than the measurement of vapor density, so that the former number is more trustworthy than the latter.

To find the equivalent of the element, that is, the amount combined with 79.92 parts (the atomic weight) of bromine, we have the proportion $70 : 30 :: 79.92 : x$, from which $x = 34.3$. The atomic weight must be this, or some small multiple of it.

The G.M.V. of air weighs 28.95 g. (pp. 34, 91). Hence the same volume of the vapor of this bromide, which is 11.8 times as heavy as air, will weigh 28.95×11.8, or 341.6 g. This is therefore the molecular weight of the compound.

. Now 30 per cent of this is the new element:

$$341.6 \times 30 \div 100 = 102.5.$$

Now 34.3 parts of the element combined with 79.92 parts of bromine. Evidently the atomic weight of the element is $3 \times 34.3 = 102.9$, the difference being due to error in determining the density. So long as no other volatile compound is known, we adopt this as the atomic weight. The rest of the molecular weight (239 parts $= 3 \times 79.92$) is bromine. Thus the formula of the compound is $ElBr_3$, and from this we see that the element is **trivalent**.

In case no volatile compound of the element can be formed, the weight combining with 79.92 parts of bromine is measured as before. Then some of the free simple substance is made, say by electrolysis, and its specific heat is determined. The sp. ht. is about 0.063. Application of Dulong and Petit's law then gives the atomic weight. The product 34.3×0.063 is equal to 2.161. Hence, the equivalent must be multiplied by 3 to give the atomic weight, for this raises the product to 6.48, which is within the limits. Thus the value of the atomic weight is 102.9, as before.

A Suggestion. — Having just discussed the conception of valence, we have now considered all the more important general laws of chemical composition. At this point the reader should pause to take breath and *review thoroughly the subjects of the first ten chapters*. The understanding of the fundamental principles which this retrospect will give will greatly lighten the task of understanding the new and more complex substances we shall have to consider, and the new kinds of reactions and new conceptions we shall encounter, in the chapters immediately following.

Exercises. — 1. Mark the valences in the formulæ: $InCl_3$, V_2O_5, OsO_4, $PtCl_4$.

2. Mark the valences of the radicals in the formulæ: $Zn(SeO_4)$, $Al_2(TeO_4)_3$, $H_3(AsO_4)$, $H(SbO_3)$.

3. If 26 g. of chromium displace 1 g. of hydrogen from hydrochloric acid, what is the valence of chromium in this displacement (see Table of Atomic Weights)?

4. Correct the following formulæ: $CaNO_3^1$, $CaPO_4$, $Al(PO_4)_2$, LiO, PbF, $Bi(NO_3)_2$.

5. One gram of a quadrivalent element unites with 0.27 g. of oxygen. What is the atomic weight of the element?

6. What are the valences of the elements in the following: LiH, NH_3, SeH_2, BN?

7. What are the valences of the metals and radicals in the following: HNO_3, $Pb(NO_3)_2$, $Ce(SO_4)_2$, KCl, $KMnO_4$ (potassium permanganate)? Name all the substances in 6 and 7.

8. What is wrong with the statement: The valence of oxygen is two because the molecular formula is O_2?

9. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element, so far as investigation of this one substance can give it (p. 134)? What is its valence?

CHAPTER XI

SOLUTION

THE property that many substances have of dissolving in others is a most interesting and valuable one. The value lies chiefly in the fact that some substances are easily soluble in a given liquid and others are, practically, not soluble in it at all. These differences in solubility enable us to accomplish, both in the laboratory and in chemical industry, many things otherwise impossible. Thus, we separated sulphur from iron (p. 17), by using carbon disulphide (CS_2) to dissolve the former. In the same way the *refining of silver* (its separation from the lead in which it is contained) is carried out on a large scale in actual practice by the use of *molten zinc* as a solvent. We must first learn precisely what is meant by a solution, and then we shall be ready to understand the uses and properties of solvents and solutions.

Solution. — We distinguish carefully between a solution and a mere mixture, also between a solution and a compound.

A mechanical *mixture,* such as that of iron and sulphur, can never be perfect, as will be evident from what has been said in an earlier chapter (p. 91) regarding the size of molecules. However finely we may powder up such a mixture, we cannot possibly bring about a sufficiently intimate dispersion of the particles of its components among one another to justify us in believing that the whole mass has become homogeneous in its ultimate structure. In any true *solution,* however, intermingling of the particles of the separate components down to molecular magnitudes has actually been accomplished. In a solution of salt in water, for example, the dissolved substance is completely and permanently dissipated throughout the liquid. However long the solution is allowed to stand, salt never settles out. Only by evaporating off all the water can a complete separation be effected.

Practically speaking, there is no limit to the amount of dissipation which may thus be produced. Thus a single small crystal of potassium permanganate, a common disinfectant which gives a very deep purple solution in water, may be dissolved in a liter or even in a hundred liters of water, and the purple tinge which it imparts to the liquid will still be perfectly perceptible in every portion of the solution. We may note here the distinguishing characteristic of a solution as opposed to a *compound*. Compounds contain definite proportions by weight (p. 23) and simple atomic ratios (p. 98) of their constituent elements. The composition of a *solution*, on the other hand, can within certain limits (see p. 140) be varied continuously.

Sometimes, when we shake up a finely-divided solid with a liquid, the latter becomes dull, or cloudy, or muddy. The solid particles are here simply suspended in the liquid, not dissolved, and will eventually settle out. Sand, shaken with water, settles at once. Flour, mixed with water, settles more slowly. The particles of flour can be readily separated from the water, however, by filtration (p. 17), the flour remaining on the paper while the water runs through. Such mixtures are called **suspensions**.

In exceptional cases, the subdivision of a suspended substance in a liquid, while not approaching molecular magnitudes, is so minute as to make its retention by filter-paper impossible, or even to prohibit it from settling out in any reasonable time. Solutions of soap, starch and gelatine in water are of this nature. Such suspensions are known as **colloidal suspensions**. To the unaided eye they appear to be true solutions. Their main properties, however, are essentially different from those of true solutions, as will be seen later (pp. 553-554).

Milk owes its cloudy, white appearance largely to droplets of oily matter, which reflect much light from their surfaces. They pass easily through filter-paper. But when milk is allowed to stand they slowly rise to the top, being lighter than the water in which they are not dissolved, but suspended. A mixture of two *liquids* of this nature is called an **emulsion**.

The characteristics, therefore, of a true solution are absence of settling or separation, homogeneity, and extremely minute subdivision (down to molecular magnitudes) of the dissolved substance.

.**The Scope of the Word.** — The word solution is used for other systems than those containing a solid body dissolved in a liquid. Thus, liquids also may be dissolved in liquids, as alcohol in water. Again, if we warm ordinary water, bubbles of gas appear on the sides of the vessel before the water has approached the boiling-point. They are found to be gas derived from the air. Agitation of any gas with water results in the solution of a large or small quantity of the gas, and heat will usually drive the gas out again. It appears therefore that **solids, liquids, and gases can equally well form solutions in liquids.**

The adsorption of hydrogen by palladium (at all events after a certain point), and by iron, takes place in accordance with the same laws as the solution of solids in liquids, and the results may be described therefore as true solutions. Liquids are in some cases absorbed by solids, and homogeneous mixtures of solids with solids are perfectly familiar. The sapphire is a solution of a small amount of a strongly colored substance, in a large amount of colorless aluminium oxide. It may therefore be stated that **solution of gases, liquids, and solids in solids appears to be possible.** ● Chemists commonly call the dissolved substance the **solute** and the substance in which it is dissolved the **solvent.** In many cases, however (when we take two liquids such as alcohol and water, for example), the terms solvent and solute are interchangeable. Gases, liquids, and solids may all be solutes, and dissolve in suitable gaseous, liquid, or solid solvents. In the present chapter only liquid solvents will be considered, and most attention will be paid to water.

Solvents. — Water is by far the commonest and most useful solvent. Very many inorganic substances dissolve in it easily. The fact that many (like sulphur and sand) do not, enables us to separate the components of a mixture containing a soluble and an insoluble substance.

Many organic substances, such as fats, paraffin, petroleum, tar, rubber, cotton, paper, shellac, and so forth, do not dissolve to any measurable extent in water. But fats dissolve readily in ether ($C_4H_{10}O$), in carbon disulphide (CS_2), in carbon tetrachloride (CCl_4), and in chloroform ($CHCl_3$). For this reason

these substances remove grease which has accidentally got into cloth. Paraffin, petroleum, and tar dissolve in gasoline (petrol), and in benzene (C_6H_6). Cotton and pure paper (like filter paper) will dissolve in concentrated sulphuric acid. Alcohol (C_2H_6O) dissolves shellac (to make varnish).

Again, water dissolves little carbon disulphide, chloroform, carbon tetrachloride, gasoline or benzene. But it dissolves alcohol in any amount, and ether in limited quantity. Some organic substances, like sugar, dissolve easily in water, but hardly at all in the other solvents just mentioned. Hence candy or molasses can be taken out of cloth by water, but not by solvents for fats.

Saturation. — As a rule, not more than a certain amount of a large bulk of solute is dissolved by a given limited quantity of the solvent. By shaking excess of the solute in a finely divided state with the solvent for a sufficient length of time, this maximum amount will finally be dissolved. The solvent is then said to be **saturated** by the solute in question. Thus, 100 c.c. of water at 18° will dissolve as much as 6.6 g. of potassium chlorate, but not more. The same amount of water will dissolve 213.4 g of silver nitrate, however, before the solvent becomes saturated. On the other hand, a saturated solution of chalk (calcium carbonate) in water will contain only 0.0013 g. in 100 c.c.

To describe these cases we should say that potassium chlorate is only moderately soluble in water, silver nitrate very soluble, and marble **insoluble.** No substance is *absolutely* insoluble, but for the sake of brevity we call substances like chalk "insoluble" because in most connections they may be so considered.

The number of grams of the solute required to saturate a fixed *volume* or a fixed *weight*, say 100 c.c. or 100 g., of the solvent we call the **solubility** of the substance (at the existing temperature). The **solubilities** at 18° of **one hundred and forty-two substances in 100 c.c. of water** are given in a **table** printed **inside the cover, at the front of this book.** A few additional examples are given below (p. 146).

In some cases there is no limit to the solubility, and therefore no possibility of the solution reaching saturation. Thus alcohol or glycerine and water will dissolve in one another in any propor-

tion. Such pairs of substances are said to be **miscible in all proportions.**

Dilute and Concentrated Solutions. — A dilute solution is one containing little dissolved matter, whether the matter is naturally very soluble or not. A concentrated solution is one containing much of the dissolved substance, and such a solution can be made with very soluble solutes only.

The only method of recognizing with certainty whether a nonvolatile solid is soluble in a liquid or not is to filter the mixture and evaporate a few drops of the filtrate on a clean watch-glass. For learning **how much** of the substance is contained in a given solution, a weighed quantity of the solution is evaporated to dryness and the weight of the residue determined.

It must be stated explicitly that in going into *solution*, as we have used the term, a compound dissolves as a whole and, if the compound is pure (p. 6), any residue has the same chemical composition as the part which has dissolved. If the residue is a different substance, a chemical interaction with the solvent has occurred. If, on evaporation, a different substance remains, there has also been chemical action.

The amount of the substance which has been dissolved by a given quantity of the solvent is described as the **concentration** of the solution. The *partial* removal of the solvent (as by evaporation) is called **concentrating,** its total removal **evaporating to dryness.** Note that a saturated solution need not also be a concentrated one. It will be very dilute, if the solute is but slightly soluble.

Units Used in Expressing Concentrations. — The concentrations of solutions, saturated and otherwise, are sometimes expressed in physical, and sometimes in chemical, units of weight. When **physical units** are employed, we give the number of grams of the solute held in solution by a fixed weight, usually one hundred grams of the solvent.

When **chemical units** of weight are employed, two different plans are possible, and both are in use. Either the equivalent (p. 134) or the atomic weights may be taken as a basis of meas-

urement. In the former case, the solutions are called **normal solutions**, and it the latter, molar solutions.

A **normal solution contains one gram-equivalent of the solute in one liter of solution** (*not* in 1 l. of solvent). The word "equivalent" has been used hitherto only of elements, and this application of the expression involves an extension of its meaning. **An equivalent weight of a compound is that amount of it which will interact with one equivalent of an element.** Thus, a formula-weight of hydrochloric acid HCl (36.468 g.) is also an equivalent weight, for it contains 1.008 g. of hydrogen, and this amount of hydrogen is displaceable by one equivalent weight of a metal. A formula-weight of sulphuric acid H_2SO_4 (98.076 g.), however, contains two equivalents of the compound, and a formula-weight of aluminium chloride $AlCl_3$ (133.38 g.) three equivalents. Hence normal solutions of these three substances contain, respectively, 36.468 g. HCl, 49.038 g. H_2SO_4, and 44.46 g. $AlCl_3$ per liter of solution. The special property of normal solutions is, obviously, that equal volumes of two of them contain the exact proportions of the solutes which are required for complete interaction. Solutions of this kind are much used in quantitative analysis. We frequently use also decinormal or one-tenth normal solutions (0.1 N or $N/10$), and seminormal (0.5 N or $N/2$), and six times normal solutions (6 N), and so forth.

A **molar solution contains one mole (gram-molecular weight) of the solute in one liter of solution** (*not* in 1 l. of solvent). When molecular formulæ (p. 116) are used, this means one gram-formula weight per liter. In the cases cited above, the molar solution contains 36.468 g. HCl, 98.076 g. H_2SO_4, and 133.38 g. $AlCl_3$ per liter. As will be seen, the concentrations of molar and normal solutions are necessarily identical when the radicals are univalent.

Weight-normal and *weight-molar* solutions are occasionally employed in the study of certain physical properties of aqueous solutions (see pp. 153-155 below). These contain one gram-equivalent weight and one gram-molecular weight, respectively, of solute in *1000 grams of water*.

Densities of Solutions. — The density or specific gravity of an aqueous solution is usually greater than that of water and,

in each case, varies with the concentration. For commercial purposes, the concentrations of solutions are commonly defined by the specific gravity. Thus, we purchase ammonium hydroxide solution of "0.88 sp. gr.," containing 35 per cent of ammonia, or sulphuric acid of "1.84 sp. gr.," containing 94.8 per cent of the acid.

The commonly greater density of a solution is utilized in making solutions in chemical factories. Shaking several tons of the mixture is out of the question, and stirring costs money. If the solid is placed in the bottom of the tank, under water, a saturated solution is formed in the lowest layer of the water, and passage of the dissolving substance into the upper layers, by diffusion, would take months or years. Hence most of the solid would remain undissolved. But when the solid is placed on a *shelf* near the surface of the water, the solution sinks through the water, fresh water rises to the shelf, and a circulation is started. This results in the dissolving of the whole material in a surprisingly short time, with no expenditure of labor whatever.

FIG. 51.

Diffusion in Solution. — It was mentioned in the preceding paragraph that diffusion of a dissolved substance in aqueous solution was an exceedingly slow process. Nevertheless, it is easy to show that, if we place a quantity of the pure solvent (Fig. 51) above a concentrated solution of a substance, and then set the arrangement aside, the dissolved body slowly makes its way through the liquid (Fig.
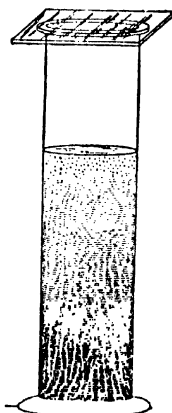
FIG. 52.

52), obliterating the original plane of separation. Eventually the dissolved body scatters itself uniformly through the whole. In other words, the molecules of the dissolved substance must be

in rapid motion in the solution, although their rate of dispersion is much impeded by the close packing of the solute molecules with which they are continually colliding.

These solvent molecules are also in rapid motion in the solution, as we saw in the discussion of the properties of liquids in the light of the kinetic-molecular hypothesis (p. 77). A careful consideration of the ultimate structure of solutions shows, indeed, that the characteristics of solvent and solute molecules *while in the solution* are in no way different (as may best be seen, by taking the case of a solution with two liquid components, such as alcohol and water), and we may therefore regard the molecules of a substance dissolved in a liquid as themselves also existent in the *liquid state*. This conception, we shall find, will be of considerable assistance to us in discussing other physical properties of solutions.

Is Dissolving a Physical or a Chemical Change? — This is a question still much discussed amongst chemists. The general view is that in a few simple cases, like dissolving paraffin in gasoline or benzene, the process may be considered purely physical, and the solution contains *both* components in unchanged chemical condition.

This opinion is based upon the fact that, when the two components of the solution are mixed in the liquid state, there is no observable heat effect or volume change on admixture, and the properties of the solution are all intermediate between those of the two pure substances, exactly as in the case of mixtures (p. 6). If one of the substances is added to the other as a solid or a gas, then the heat absorbed or evolved is practically identical with the heat required to melt the same quantity of the solid, or with the heat liberated in the condensation of the same quantity of the gas. Such solutions are called "**ideal solutions.**"

On the other hand, when water is used, as it is more frequently than any other solvent, chemical changes undoubtedly take place. The water itself, at least, is always changed. Water *in the liquid state* is not simply H_2O. Its physical properties indicate that it is an *associated* liquid, extensive combination

having taken place between simple H_2O molecules to form more complex molecules with the general formula $(H_2O)_n$. Dissolving *any* substance in water must upset the equilibrium (p. 78) amongst these different kinds of molecules:

$$(H_2O)_n \rightleftarrows nH_2O$$
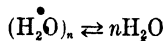
and produce more of one and less of the other kind. This is the extent of the chemical change in the water alone.

The dissolved substance combines also, in the majority of cases, with part of the water. In a great many instances certain of the compounds formed can be definitely isolated from the solution, as, for example, in the case of hydrates such as Na_2SO_4, $10H_2O$ or $CuSO_4,5H_2O$. In other examples the exact nature of the compounds present in solution is often more difficult to determine, and no simple statement can as yet be made about them. But the compounds, whatever they are, are physically dissolved in the rest of the water and may be regarded as existent in the solution *in the liquid state,* just like any unchanged solute.

Dissolving, therefore, is partly a chemical, and only partly a pure physical process. The striking differences in solubility already mentioned (p. 140) may consequently be accounted for partly on a chemical, and partly on a physical basis. The main *chemical* factor is compound formation between the components of the solution. The more extensive this is, the greater, in general, is the solubility. Thus substances which form definite hydrates with water are mostly extremely soluble, while substances which are only difficultly soluble in water invariably crystallize out from an aqueous solution in an anhydrous state. The main *physical* factor is the relative magnitude of the cohesive forces between the various types of molecules present in the solution. Thus in the case of water and benzene, the water molecules attract one another much more strongly than they do the benzene molecules. Molecules of benzene endeavoring to intermingle with water molecules encounter, therefore, very considerable resistance, and are almost certain to be squeezed out. The two liquids, indeed, are found to be practically immiscible.

Temperature

Fig. 53.

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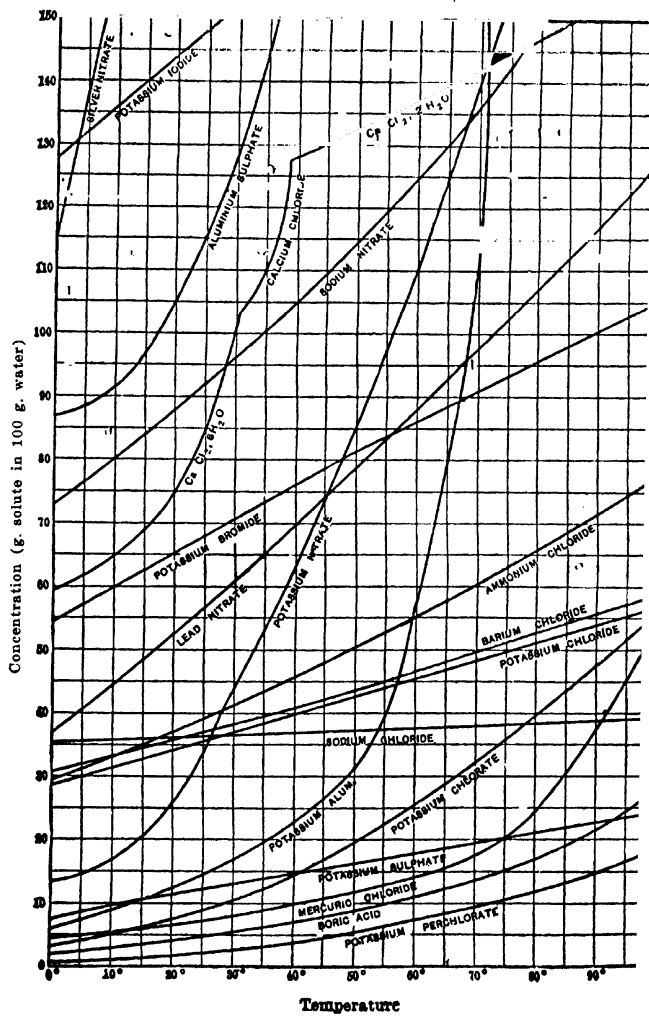
Influence of Temperature on Solubility. — The quantity of a substance which will dissolve in a fixed amount of a given solvent depends very largely upon the temperature. Usually the solubility of solids in liquids increases with rise in temperature. Measurements may be made by the method described before (p. 141), using *excess* of the finely powdered solute with different portions of the same solvent in vessels kept at different temperatures. The most useful way of representing the results is to plot them graphically. The diagram (Fig. 53) shows the curves for a few familiar substances. The ordinates represent the number of grams of the anhydrous compound which is dissolved by 100 g. of water in each case. The abscissæ represent the temperatures. The concentration for any temperature can be read off at once. Thus, 100 g. of water dissolve 13 g. of potassium nitrate at 0° and 150 g. at 73°. The increase in solubility is here enormous. On the other hand, the same quantity of water will dissolve 35.6 g. of sodium chloride at 0° and 39 g. at 100°. The difference is shown at once when we examine the curves and observe that the line representing the solubility of sodium chloride scarcely rises at all between 0° and 100°, while that of potassium nitrate is extremely steep.

Cases in which the solubility of solids in liquids decreases with rise in temperature are less common. The solubility of slaked lime (calcium hydroxide $Ca(OH)_2$, used to make lime-water) is 0.175 g. at 20° and 0.078 g. at 100°. Anhydrous sodium sulphate Na_2SO_4 (Fig. 54, p. 150) is another illustration of this point.

When two liquids are not completely miscible, their solubilities in each other are also found, in the majority of cases, to increase with rise of temperature. Thus 100 g. of water will dissolve only 8 g. of phenol at 10°, and 100 g. of phenol will dissolve only 33 g. of water at the same temperature, but above 68.3° the two liquids are miscible *in all proportions*. In a few cases, however, the solubility increases with decrease of temperature. For example, 100 g. of water will dissolve only 5 g. of ether at 30°, but at 0° the solubility has risen to 13 g.

The solubility of gases in liquids *always* diminishes with ris-

ing temperature. This may be illustrated by heating cold tap-water in a beaker, when the dissolved gases, originally obtained from the air, are driven out in bubbles as the boiling-point is approached (compare p. 139).

Crystallization. — If the solvent has been saturated while warm, and the dissolved substance is one that is less soluble at lower temperatures, then, when the temperature is allowed to fall and the merest trace of solute is introduced, the solute begins to come out of solution. The amount appearing, of course, is only the **excess** beyond what is needed to saturate the solvent at the lower temperature.

If the solute is a liquid, it appears at first as a cloud of drops, rendering the solution milky. This may be shown by cooling a solution of phenol in hot water.

If the solute is solid, then the particles, as they appear, take the form of **crystals** (p. 105). These *grow* by taking on more of the separating solute. If the cooling goes on slowly, very large crystals can finally be obtained. On the other hand, with rapid cooling, new crystals are continually formed, and a fine crystal-meal falls to the bottom of the solution. The crystals in this meal, however, when viewed through a lens, are seen to be just as perfect as the larger ones.

When a more dilute solution is used, instead of a saturated one, crystals may still be obtained. A *part* of the solvent must first *be removed*, however. This may be done, either by boiling the solution for some time, or by leaving it to evaporate in a wide dish in which a large surface is exposed.

When the dissolved substance forms a compound with the solvent (*e.g.*, a hydrate, see p. 84) which is less soluble than the original solute at the temperature of crystallization, the crystals are composed of this compound.

The *whole* of the solvent may be boiled off. But in this case good crystals of the solute are never obtained — the residue is usually a crust composed of imperfect crystals.

When the substance is more soluble in cold than in hot water, then crystallization is produced by raising the temperature of the saturated solution.

Crystallization from a Melted Mass. — In this connection, it should be noted that there is another way of obtaining crystals. This is to *melt* the substance (without any solvent), and allow the mass to cool slowly. When a part has solidified, the rest of the liquid is rapidly poured off. Metals and many other fusible substances give good crystals in this way. Water itself, when it freezes, deposits radiating, hexagonal crystals of ice

Supersaturation. — When a hot, saturated solution is cooled in the *absence* of any undissolved solid, there is quite commonly some delay before the crystals begin to appear. The solution, pending the appearance of the crystals, is then said to be **supersaturated.** In most cases the crystals soon appear in due course, especially if the liquid is shaken or stirred. But certain substances have a tendency to remain indefinitely in the state of supersaturated solution. The hydrates of sodium sulphate $(Na_2SO_4, 10H_2O)$ and of sodium thiosulphate (photographers' "hypo" $Na_2S_2O_3, 5H_2O$)· give solutions in water of this nature. The addition of a minute crystal of the substance concerned ("inoculation"), however, always starts the crystallization.

Many pure liquids, similarly, when cooled below their freezing-point, do not always crystallize out at once. Thus water can be taken down to $-10°$ without the appearance of ice. In this condition it is said to be *supercooled.* Shaking, or stirring, or (better still) *inoculating* with a fragment of ice, induces crystallization in this case also. It may be noted that the opposite phenomenon has never been observed; ice invariably melts sharply at $0°$ under atmospheric pressure.

A very striking illustration of crystallization from a super-saturated solution may be obtained by saturating water with anhydrous sodium sulphate Na_2SO_4 at, say, $50°$, at which temperature 100 g. of water hold in solution 40 g. of Na_2SO_4 (Fig. 54). The excess of the solid is carefully and completely separated from the liquid, and the latter is allowed to cool, say to $15°$, in a flask loosely stoppered with cotton. The solution now contains a much smaller amount of sodium sulphate (Na_2SO_4) than at its present temperature it could acquire from contact with anhydrous sodium sulphate (62 g. at $15°$, see dotted curve in the diagram).

It is, therefore, impossible for the solution to deposit crystals of this substance, with respect to which it is now unsaturated. On
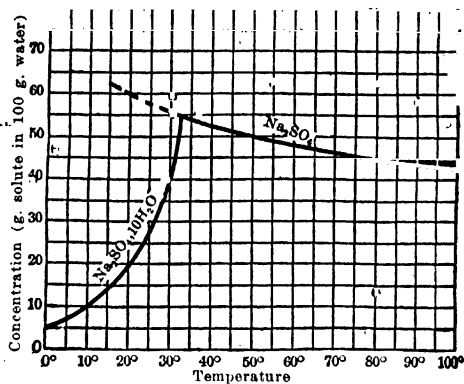
FIG. 54.

the other hand, it contains a much larger amount than it could acquire from contact with crystals of hydrated sodium sulphate

FIG. 55.

$Na_2SO_4,10H_2O$ (13 g. at 15°). It is therefore highly supersaturated with respect to this substance. Yet in the absence of a crystal of the hydrated salt, no deposition of the dissolved substance begins. The solution may be kept indefinitely without alteration. The introduction, however, of the minutest fragment of the decahydrate at once starts the crystallization, the added crystal forming the center of a radiating mass of blade-like crystal clusters, which sprout with astonishing rapidity through the liquid (Fig. 55).
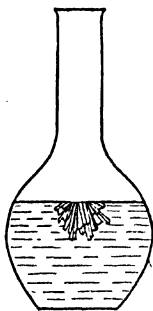
Heat of Solution. — The process of solution, in the case of most solid substances, absorbs heat, so that the solution becomes cooler as the crystals dissolve. Conversely the process of crystallization usually evolves heat. Thus, in the cases of Na_2SO_4, $10H_2O$ and $Na_2S_2O_3,5H_2O$ mentioned above, when the crystalliza-

tion is brought about in the cool, supersaturated solutions, the rise in temperature is considerable.

This fact has been utilized in devising a sort of hot-water bottle. The bottle is made of rubber and contains a super-saturated solution of sodium acetate. Whenever the heat is wanted, the stopper is taken out, rubbed with the finger, and screwed back. The rubbing spreads on the inner surface of the stopper, next the liquid, some of the crystals adhering to the screw, and so starts the crystallization. The bottle then becomes warm and remains so for a considerable time. After it has cooled, it is placed, without being opened, in boiling water to redissolve the crystals, and, when cold, is ready for use again.

The solution of sulphuric acid in water is attended by an exceptionally large evolution of heat. One formula-weight of the pure acid, dissolving in a practically unlimited volume of water, liberates 39,170 calories. The solution of one formula-weight of sodium sulphate decahydrate in water, on the other hand, under the same conditions, *absorbs* 18,760 calories.

In both of the above cases, the magnitude of the heat effect varies considerably with the concentration of the solution. This is due to the fact that extensive chemical changes take place in the process of solution. With some salts in water (see cupric chloride, p. 219) the heat effect may even change in sign as the solution approaches saturation. Such solutions are evidently very far from *ideal*, since the heat absorbed in dissolving a formula-weight of a solid in an ideal solvent is identical with the molecular heat of fusion of the solid (p. 144), whatever the concentration of the solution.

The heat change involved in dissolving one formula-weight of a substance in a practically unlimited volume of its practically saturated solution is, we shall find in a later chapter (p. 217), a very important quantity. It is known as the **heat of solution.**

The Physical Properties of Solutions. — The physical properties of a solution depend, in all cases, upon its *concentration,*

i.e., upon the relative amounts of solvent and of solute present, The more concentrated the solution, the more will its physical properties, in general, differ from that of the pure solvent. The observed changes may be divided into two classes.

In the first class, the amount of the change varies with the substance dissolved. Very striking and difficult to explain, for example, are the erratic changes **in volume** which occur when solution takes place. Specific effects of this class show that chemical changes often accompany solution. For example 58.5 g. of sodium chloride (volume 27.5 c.c.) and 10,000 c.c. of water have, separately, a volume totalling 10,027.5 c.c., but, when they are brought together, the solution measures only 10,016.5 c.c. This is a very dilute solution (about ½ per cent), so that the contraction of 11 c.c. is relatively considerable. On the other hand, 214 g. of ammonium chloride (volume 142.5 c.c.) and 843.5 c.c. of water have a total volume of 986 c.c., but when brought together give 1000 cc. of solution. Here there is an expansion of 14 c.c. In the case of table-sugar and water, however, there is almost no change in volume.

Another important property of solutions in which the influence of the solute is *specific* is **conduction of electricity.** Pure water is an exceedingly poor conductor. A solution of table-sugar in water is also practically non-conducting. But when acetic acid is dissolved in water a solution is obtained which conducts the current fairly well, while a solution of sodium chloride is an exceedingly good conductor. The significance of these differences in behavior will be taken up later (p. 226).

In the case of many properties of solutions, however, it has been found that *equal numbers of dissolved molecules of different substances produce the same amount of change.* The effect appears here to be due essentially to physical causes, even although the solutions may not be strictly ideal, and is discussed in the following sections in the light of the molecular hypothesis. Before attacking these sections, the student is recommended to refer back to pp. 77-79 and read these pages through again carefully, noting that the equilibrium relationships between liquid water and water vapor, therein discussed, can obviously be extended to any volatile substance in contact with its own vapor.

Vapor Pressure of Solutions. — When we take equal quantities of a volatile liquid (*e.g.*, benzene, C_6H_6) and add to each equal *weights* of different non-volatile solutes (*e.g.*, naphthalene, anthracene, camphor; three organic solids which are relatively non-volatile at ordinary temperatures) we find that the vapor pressures of all the resulting solutions are less than that of the pure solvent, but the depression is different in each case. But if, instead of adding equal *weights* of the different solutes, we add equal *numbers* of *molecules* (as we can do by dissolving, for example, 1 g. molecular weight of each substance in 1000 g. of benzene), we find that *the depression is the same in every case. The depression is proportional, moreover, to the fraction of solute molecules in the solution* (**Raoult's Law**). This very striking fact is explained by the molecular hypothesis as follows:

Every molecule at the surface of a pure volatile liquid has an equal chance to escape into the vapor above the liquid. But as soon as we add to such a liquid a solute which is practically non-volatile, we have a liquid in which some of the molecules have no tendency to pass into the state of vapor, but are *fixed* in the liquid state. Suppose, for instance, we consider a solution in which one molecule in every ten is non-volatile; the intensity of the hail of molecules leaving the liquid will evidently be reduced by one-tenth. Equilibrium between liquid and vapor over such a solution will be re-established only when the intensity of the hail of vapor molecules returning to the liquid is also reduced by one-tenth, since otherwise more molecules will be returning than leaving. This means that the vapor pressure of the solution must be one-tenth less than that of the pure solvent.

It is important to note that the *nature* of the solute is here immaterial, the essential factor is the number of molecules it furnishes to the solution. We have here a method of determining *the molecular weights of non-volatile substances.* By dissolving a known weight of such a substance in a known weight of a suitable solvent and determining the *relative depression of vapor pressure* thereby produced, we learn what fraction of the molecules in the solution belong to the solute, and hence can calculate its molecular weight.

All aqueous solutions show a lower tension of water vapor

than does pure water. With *conducting* solutes (*e.g.*, sodium chloride), indeed, the vapor pressure depressions obtained are abnormally large, and do not agree with the accepted molecular weights. This is a point to which we shall return later (p. 228).

If a substance is very soluble in water, the solution may give a vapor pressure of water less even than that commonly present in the atmosphere. Such a solution, placed in an open vessel, will not evaporate. On the contrary, it will take up moisture from the air and increase in bulk. For this reason very soluble substances are commonly moist and, when exposed to the air, extract water from the latter and dissolve in this water. This behavior is called **deliquescence**, and is shown, for example, by the hydrate of calcium chloride $CaCl_2,6H_2O$, used to dry gases (p. 70).
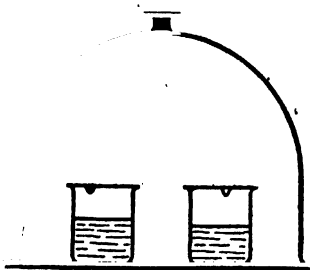
The principle involved will become clear if we imagine two vessels, one containing pure water and one an aqueous solution, to be placed on a glass plate and covered by a bell jar (Fig. 56). Each liquid exchanges water molecules with the moist air in the jar, but the solution gives off water more feebly than does the pure water. The result is that the latter can produce a pressure of water vapor higher than that which would be in equilibrium with the solution. The solution, therefore, receives continuously more molecules than it emits, and increases in volume. The pure water thus gradually passes through the vapor state into the solution until it is all gone. If sufficient water was present, the process would go on until the solution became infinitely dilute. •

Boiling-Points of Solutions. — The boiling-point of a liquid is that temperature at which the vapor pressure reaches 760 mm. (see p. 74). Since the addition of a non-volatile solute lowers the

vapor pressure of a pure liquid, it naturally *raises the boiling-point* to a higher temperature.

In dilute non-conducting solutions, equal numbers of molecules of different solutes raise the boiling-point of a given solvent to the same extent. Thus, one molecular weight of sugar $(C_{12}H_{22}O_{11} = 342$ g.) or of glycerine $(C_3H_8O_3 = 92$ g.), dissolved in 1000 g. of water, will each raise the boiling-point from 100° to 100.52°.

Molecular weights of non-volatile, non-conducting substances can therefore be determined by finding out what weight of the substance, when dissolved in 1000 g., is required to raise the boiling-point of water from 100° to 100.52°.

Freezing-Points of Solutions. — The addition of a solute similarly tends to prevent the *freezing* of the solution, for freezing means the separation of a part of the *pure solvent* in the form of ice. Hence solutions can be frozen only at temperatures *below* those of the pure solvents. Thus, one molecular weight of a substance such as sugar (342 g.) or glycerine (92 g.), dissolved in 1000 g. of water, will cause the water to freeze at −1.86° instead of 0°. Molecular weights can be measured by this method also.

This behavior explains why sea water is frozen in cold weather much less often than fresh water.

It explains also *why salt thrown on ice will cause the latter to melt.* Saturated salt solution freezes only at −21°, to give a mixture of pure ice and pure $NaCl,2H_2O$, both in solid form. Hence, ice and salt cannot permanently exist together *above* that temperature. When the outside temperature is below −21°, salt will no longer melt the ice. But calcium chloride, which is more soluble, will do so. A mixture of ice and salt, giving the temperature −21°, is called a **freezing mixture**. Such a mixture is used in freezing ice cream and ices.

Definition of a Saturated Solution: A Warning. — To avoid a common **misconception,** it must be noted that solution is *not* a process of filling the pores of the liquid. If that were true, approximately equal weights of all substances would find accom-

modation in equal volumes of water. The fact is that, for example, 100 c.c. of water will dissolve 195 g. of silver fluoride, but only 0.00000035 g. of silver iodide, although the space available (if there *is* any such space) is the same in both cases.

The same conclusion is reached when we consider that a simple salt and its various hydrates all have *different* solubilities, although the solutions which they give in water are identical. Thus, at 20°, $Na_2SO_4, 10H_2O$ will give about 18 g. of Na_2SO_4 to 100 c.c. of water. But *anhydrous* sodium sulphate Na_2SO_4 at 20° gives 59 g. to the same amount of water.

The reader is also warned against the frequent definition of a *saturated solution* as one containing all of the solute that it *can hold.*; A supersaturated solution evidently, holds more. The saturated solution under any given conditions is *that solution which, when placed in contact with excess of the solute, is found to be in equilibrium.*

The molecular hypothesis may again be called to our assistance in this connection. When we have a solute (either crystalline, or liquid, or gaseous) in contact with its saturated solution, and therefore in equilibrium with it, two opposing tendencies must balance each other at the surface of contact. One of these is the tendency of the solute particles to escape into solution, the other is the tendency of the solute particles already in solution to return back to the solute. The first of these tendencies (the intensity of the hail of particles thrown off from the surface of the solute into a given solvent, under given conditions of temperature and pressure) we may regard as constant. The second tendency (the intensity of the hail of particles returning from the solution to the surface of the solute) will increase steadily as the concentration of the solute particles in the solution increases. At one definite concentration only, therefore, can these two opposing tendencies counterbalance, namely that of the *saturated solution.* The rate at which solute particles are returning from the solution just equals, in this case, the rate at which they are entering. With *unsaturated* solutions, containing *less* solute, the number of returning particles will be deficient, and the solute will continue to dissolve until it all disappears or saturation is reached. With

supersaturated solutions, on the other hand, containing *more* solute, the number returning will be in excess, and deposition of home-coming particles on the solute surface will continue until this excess is wiped out.

If, however, we have a supersaturated solution in which no free solute is present, the solute particles in the solution have no home to return to, no surface upon which they can deposit themselves. They are therefore compelled to continue wandering around and around in the solution, having lost their equilibrium completely. By violent shaking or stirring we may succeed in inducing crystallization in such a solution, but the only certain means of establishing equilibrium conditions is inoculation with a small fragment of the solute.

Conditions Affecting the Solubility of a Gas. — When the dissolving substance is a **gas**, led through or confined above the liquid at a definite pressure, the gas dissolves until a state of equilibrium between dissolving and emission is reached, for example, Oxygen (gas) $\rightleftarrows$ Oxygen (dissolved), and the liquid is then saturated with the gas.

It is found, as the molecular theory would lead us to expect, that **the concentration of the saturated solution of a gas is proportional to the pressure at which the gas is supplied (Henry's law).**

This equilibrium, Gas (gaseous) $\rightleftarrows$ Gas (dissolved), can be reached, naturally, from the other direction, namely by starting with a solution of the gas and a space above the solution containing, at first, none of the gas. The gas leaves the solution until the rates of emission and return become equal. Hence, a gas may be entirely removed from solution by bubbling a foreign gas through the liquid. The bubbles furnish the space to receive the emitted gas, and have a large surface, so that the process goes on rapidly. The bubbles also escape, and carry with them the emitted gas, so that, in this case, there is no re-solution. This in a case of nullifying one of the two opposed tendencies (p. 79).

When a **mixture of two gases** is shaken with a liquid, the gases behave independently of each other (**Dalton's law, p. 47**). Each

has the same pressure, and therefore the same solubility, as it would possess if it alone occupied the whole space above the liquid.

Two Immiscible Solvents: Law of Partition. — An interesting application of the same ideas may be made to a case which occurs very commonly in chemical work. If we shake up a small particle of iodine with water, we find that it dissolves slowly, giving eventually a saturated but very dilute solution. In ether, however, iodine is much more soluble. If now ether in sufficient quantity be shaken with the aqueous solution, the greater part of the iodine will find its way into the ether, and be contained in the brown layer which rises to the top. The process of removing a substance practically from solution in one solvent and securing it in another is called **extraction.** We find in such cases that neither solvent can entirely deprive the other of the whole of the dissolved substance. A state of equilibrium is finally reached: I_2 (in water) $\rightleftarrows I_2$ (in ether). The partition of the substance takes place in proportion to its solubility in each solvent **(law of partition).** If is found that any amount of the solute, up to the maximum the system can contain, provided the solute exists in the same molecular state in either solvent, is divided so that the ratio of the concentrations in the two solvents is always the same. In the case of iodine divided between water and ether, this distribution ratio is about 1 : 200.

This principle is used in Parke's process for extracting silver from molten lead, by means of molten zinc as the second solvent. It is employed in separating interesting compounds from animal secretions and vegetable extracts, and in purifying such compounds. Nicotine from tobacco and cocaine from coca leaves are secured in this way.

Exercises. — 1. Give other examples of limited solubility in various solvents (p. 140).

2. What weights of phosphoric acid (p. 83) and of sodium hydroxide, respectively, are required to make 1 liter of a normal solution?

3. Express the concentrations of solutions of ammonium

chloride, saturated at 0° (sp. gr. 1.076), and of potassium sulphate K₂SO₄, saturated at 10° (sp. gr. 1.083), in terms of a normal solution (pp. 142, 146).

4. Express the concentration of a five per cent aqueous solution of phosphoric acid (sp. gr. 1.027), in terms of a normal and a molar solution, respectively.

5. Explain why, (a) pulverization and, (b) agitation hasten the dissolving of a solid.

6. Read from the curves (p. 146) the solubilities of potassium nitrate at 15°, of potassium chloride at 30°, of potassium chlorate at 45°. What are the relative rates at which the solubilities of these salts increase with rise in temperature?

7. At what point in a tank of water should you introduce ammonia gas, in order, with the least effort, to saturate the water? The sp. gr. of the saturated solution is 0.88.

8. Give two ways of separating a mixture, consisting of a suspended solid and a liquid (p. 138).

9. If you had a spot on your clothing consisting of: (a) grease, (b) sugar, or (c) sugar and grease together, or (d) varnish, how should you proceed in each case to remove the spot?

10. If chalk (5 g.) and potassium chlorate (5 g.) were mixed, how should you separate them (p. 17)? Explain how you could secure each substance.

11. Could you make (a) a concentrated, (b) a saturated solution of chalk in water (p. 140)? Of alcohol in water?

12. If you saturated 200 c.c. of water at 70° with (a) salt, or (b) potassium nitrate, and then cooled the clear liquid to 20°, what weight of the solid substance would separate out in each case (p. 146)?

13. To make as concentrated a solution of lime water as possible, should you use hot water or cold (p. 147)?

14. Explain why boiled water has a slightly different taste from tap-water that has not been boiled (p. 80).

15. If 100 g. of a non-volatile substance, dissolved in 1000 g. of benzene (C₆H₆), lower the vapor pressure from 74.8 to 68.0 mm., what is the molecular weight of the substance? (Use Raoult's Law, p. 153.)

16. Explain why potassium carbonate becomes wet, and finally

dissolves, when exposed to moist air.   How must calcium chloric
be preserved from becoming moist?

17. If 52 g. of a substance dissolved in 1000 g. of water gives
solution boiling at 100.26°, what is the molecular weight of tl
substance (p. 155)?

18. If 68.5 g. of a substance, dissolved in 500 g. of wate
gives a solution freezing at:– 1.86°, what is the molecular weigl
of the substance (p. 155)?

19. Explain why a sodium acetate hot-water bottle can l
used over and over again.   What is the source of the heat it giv
out each time it is used?

CHAPTER XII

WE have had occasion several times to mention common salt, or sodium chloride NaCl. This is one of the most familiar chemical substances. Large quantities of it are used in the household, in cooking and in making freezing mixtures. Still larger amounts are consumed in manufacturing washing soda, caustic soda, and soap, for all of which it furnishes the necessary sodium. It is used also in preserving fish and other foods. It supplies the chlorine used in bleaching and in the sterilization of city waters. We shall consider it first as a means of making hydrogen chloride and sodium hydroxide, and shall take the opportunity in this chapter to develop the properties of these two very important substances in some detail.

Preparation of Hydrogen Chloride HCl from Salt. — When a few drops of commercial, concentrated sulphuric acid (H_2SO_4) are poured upon common salt in an open dish, vigorous effervescence begins. This indicates that a gas is forming in bubbles upon the salt and that the bubbles are rising through the layer of acid and bursting. The gas is itself invisible, but when we breathe upon the contents of the vessel, a heavy fog is produced. This is due to condensation of water vapor (in the breath) to droplets of water, in which the gas has dissolved. The fog is composed, in fact, of drops of a solution of hydrogen chloride (HCl) in water, which receives the name of **hydrochloric acid** (in commerce, muriatic acid).

In order to handle the gas more readily, the sulphuric acid may be allowed to fall from a funnel, drop by drop, upon salt contained in a flask (Fig. 57). Soon the air in the flask is all displaced by the gas, and the latter issues from the open delivery tube. If a **U**-tube containing some water is attached to the delivery tube, the gas dissolves in the water as fast as it is formed.

If the correct proportions of the materials are used, then, when the action is over, all that remains in the flask is a white solid, different from salt, and called sodium-hydrogen sulphate $NaHSO_4$.
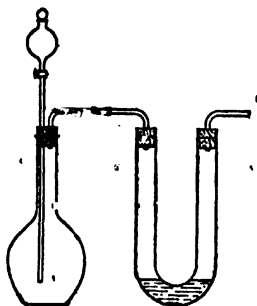
A part of this may be in solution in a little water, contained originally in the commercial sulphuric acid. The equation is easy to make from the formulæ given,

$$NaCl + H_2SO_4 \rightarrow HCl\uparrow + NaHSO_4, \quad (1)$$

and requires no further balancing. (An arrow pointing upward is used in equations to indicate that the substance to which it refers removes itself from the reaction by escaping in the form of a gas.)

FIG. 57.

The action described is the one which occurs in the laboratory. When a double proportion of salt and a high temperature are used, a second action occurs:

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl\uparrow$$
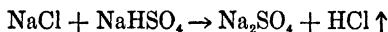
and sodium sulphate Na_2SO_4 remains. In Europe this action is employed, with furnace heat, in manufacturing sodium sulphate, from which sodium carbonate is afterwards prepared. The hydrogen chloride passes into a tower, down which water trickles over lumps of coke, and is dissolved.

Other Sources of Hydrogen Chloride. — Chlorides of other metals could be substituted for the sodium chloride in this action, and all but the less soluble ones would give hydrogen chloride freely. Common salt is employed because it is the cheapest of the chlorides.

While theoretically any acid would, like sulphuric acid, furnish the required hydrogen, and liberate hydrogen chloride, yet in practice no other acid works so well. Some, like phosphoric acid H_3PO_4, act too slowly, because they do not dissolve sodium chloride so readily. Others, like hydrofluoric acid HF, are **too**

volatile, and the heat of the action would send them over with the hydrogen chloride in the form of vapor. Others, like nitric acid HNO_3, would react chemically with hydrogen chloride. Still others, like hydriodic acid HI, could be used only in aqueous solution, and the water would dissolve the hydrogen chloride produced, and prevent its escape from the vessel. Aside from these objections, all the other acids are more expensive than sulphuric acid.

The Molecular View of the Interaction of Sulphuric Acid and Salt. — One who has used the above described methods for making hydrogen chloride without reflection would not realize the complexity of the machinery by which the result is achieved. The means are apparently very simple. Yet the mechanical features of this experiment, when laid bare, are extremely curious and interesting. A single fact will show the possibilities which are concealed in it.

If we take a saturated solution of sodium-hydrogen sulphate in water and add to it a concentrated solution of hydrogen chloride in water (concentrated hydrochloric acid), we shall perceive at once the formation of a copious precipitate. This is composed entirely of minute cubes of sodium chloride:

$$NaHSO_4 + HCl \rightarrow H_2SO_4 + NaCl \downarrow. \qquad (2)$$
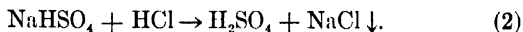
(An arrow pointing downwards is used in equations to indicate that the substance to which it refers removes itself from the reaction in the form of a precipitate.) Now this action is nothing less than the precise reverse of (1), yet it proceeds with equal success. In fact, this chemical interaction is not only **reversible** (p. 85), but can be carried virtually to completion in *either* direction. It is only in presence of a very large excess of water, sufficient to keep both the hydrogen chloride and the salt all in solution, that it stops midway in its career and is valueless for securing a complete transformation in either direction:

$$NaHSO_4 + HCl \rightleftarrows H_2SO_4 + NaCl.$$
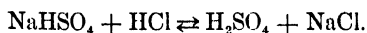
In an action which is reversible, if the *products* remain as perfectly mixed and accessible to each other as were the *initial sub-*

stances, their interaction will continually undo a part of the work of the forward direction of the change. Hence, in such a case the reaction must, and does, come to a standstill while as yet only partly accomplished; but this was not the case with actions (1) and (2). Let us examine the means by which the premature cessation of each was avoided.

In equation (1) the salt-dissolved to some extent in the sulphuric acid, NaCl (solid) $\rightleftharpoons$ NaCl (dslvd.), and so, by intimate contact of the two kinds of molecules in the resulting solution, the products HCl and NaHSO₄ were formed. On the other hand, the hydrogen chloride, being practically insoluble in sulphuric acid, escaped as fast as it was formed: HCl (dslvd.) $\rightleftharpoons$ HCl (gas). Hence, in that case, almost no reverse action was possible, and the double decomposition went on virtually to completion. With all the sodium-hydrogen sulphate in the bottom of the flask, and most of the hydrogen chloride in the space above, the two products might as well have been in separate vessels so far as any efficient re-interaction was concerned. This plan, in which water is purposely excluded, forms therefore the method of making hydrogen chloride.

In equation (2), on the other hand, the hydrogen chloride was taken *in aqueous solution,* and was mixed with a concentrated solution of sodium-hydrogen sulphate. The acid was, therefore, kept permanently in full contact with the sodium-hydrogen sulphate. It had, in this case, every opportunity to interact with the latter and no chance of escape. Every molecule of each ingredient could reach every molecule of the other with equal ease. Furthermore, the sodium chloride, produced as a result of their activity, is not very soluble in concentrated hydrochloric acid (far less so than in water), and so it came out as a precipitate: NaCl (dslvd.) $\rightleftharpoons$ NaCl (solid). But this was almost the same as if it had gone off as a gas. It meant that the greater part of the salt was in the solid form. In this form, it was no longer able to interact effectively molecule to molecule with the other product, the sulphuric acid. Hence, there was little reverse action to impede the progress of the primary one. Thus (2) is nearly as perfect a way of liberating sulphuric acid as (1) is of liberating hydrogen chloride.

Precipitation. — When two soluble substances are dissolved separately in water, and the solutions are mixed, chemical inter-action frequently is evident between the dissolved materials. If one of the products is not very soluble, then a *supersaturated solution* (p. 149) *of this product may be thus produced.* As a rule, this substance immediately becomes visible as a fine powder, called a **precipitate**, suspended in the liquid. More or less rapidly, according to its fineness of dispersion, this precipitate settles out, leaving the solution clear. Equation (2) in the preceding paragraph is an example of such a reaction.

Often the precipitated product can be recognized by the physical *appearance* of the precipitate, and so this sort of action is used as a test for one of the *original* substances. Thus, precipitates are classified according to their color. Again, precipitates of the same color differ in degree of dispersion, and may be described as **gelatinous, curdy, pulverulent, or crystalline.** In the two former cases, at least, the precipitation is so sudden that there is not time for crystals to be formed, and the product is *amorphous* (see p. 106).

Physical Properties of Hydrogen Chloride. — Hydrogen chloride is a *colorless* gas. It is sour in *taste*, and has a sharp *odor*. It is irritating, but not poisonous in small amounts.

The gas is exceedingly *soluble* in water, one volume of which, at 15°, will dissolve no less than 455 volumes of the gas. The saturated solution at 15° contains nearly 43 per cent of the gas by weight. The concentrated hydrochloric acid of commerce contains about 35 per cent.

The *density* of the gas (wt. in g. of 1 c.c.) is 0.001628. Of more interest to the chemist is the weight of 22,400 c.c. or 22.4 liters (the gram-molecular volume), namely 36.468 grams. This is the molecular weight of the substance. As we have seen (p. 93), it is made up of 1.008 g. of hydrogen combined with 35.46 g. of chlorine.

Is the gas heavier or lighter than air? This question is answered at once if we recall the fact that the 22.4-liter cube full of air weighs 28.95 g. (p. 134). The gas is one-fourth heavier. It may therefore be collected by upward displacement (Fig. 31b, p. 63).

The gas can be *liquefied* by pressure alone at any temperature below 52° (its critical temperature). One atmosphere pressure will liquefy it at −84°, which is therefore the boiling-point of liquefied hydrogen chloride. Both in the gaseous and liquefied states pure hydrogen chloride is a non-conductor of electricity.

When the *concentrated* aqueous solution is heated, it is the hydrogen chloride and not the water which is vaporized, for the most part. When the concentration has been reduced to 20.2 per cent, the rest of the mixture distils unchanged at 110°. This occurs because, at this concentration, the hydrogen chloride is carried off in the bubbles of steam in the same proportion in which it is present in the liquid. If a *dilute* solution is used, *water* is the chief product of distillation (about 100°?, but gradually the boiling-point rises and, when the concentration has reached 20.2 per cent once more, the same hydrochloric acid of **constant boiling-point** (110° at 760 mm.), as it is called, forms the residue.

Chemical Properties of Hydrogen Chloride. — In the case of a *compound,* the chemical property in regard to which we first enquire is its **stability** (p. 43). Is it easy or difficult to decompose by heating? Hydrogen chloride must be heated above 1500° before even a trace of it is dissociated into hydrogen and chlorine. Pure hydrogen chloride is therefore a *very stable* and, from a chemical point of view, rather an *inactive* substance. It has no action on *non-metals,* such as phosphorus, carbon, sulphur, etc. However, many of the more *active metals* (see p. 64), such as potassium, sodium, and magnesium, decompose it. Hydrogen is set free, and the chloride of the metal is formed.

$$2K + 2HCl \rightarrow 2KCl + H_2 \uparrow.$$
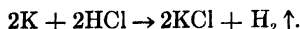
When hydrogen chloride is mixed with *ammonia* NH_3 the gases *unite* to form a cloud of fine, solid particles of ammonium chloride.

$$HCl + NH_3 \rightarrow NH_4Cl \downarrow.$$
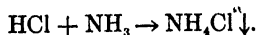
Chemical Properties of Hydrochloric Acid. — The solution of hydrogen chloride in water is an entirely different substance in its behavior from hydrogen chloride. (1) The solution is *sour*

in taste.   (2) It *changes the color of litmus,* a vegetable coloring matter, from blue to red.   (3) It is a *conductor of electricity,* and is decomposed by the current, *hydrogen being liberated* at the negative wire (p. 65).   (4) When the *metals preceding hydrogen* in the order of activity (p. 64) are introduced into hydrochloric acid, *hydrogen is displaced* and liberated.

In a later chapter (Ch. XVI) we shall see that these four properties of hydrogen chloride in aqueous solution are properties common to *all substances called acids.*   We may sum up the main properties of a solution of hydrogen chloride in water in one word, therefore, by saying that it is an **acid.**

Hydrochloric acid interacts with many other compounds in solution.   In some instances, one of the new substances produced can be seen, because it appears as a precipitate.   One such example has already been discussed in detail (see equation 2, p. 163).   When hydrochloric acid is added to a solution of silver nitrate (lunar caustic, $AgNO_3$), a precipitate of *silver chloride* (AgCl) is obtained, which is white and curdy in appearance. The other product, nitric acid (HNO_3), remains dissolved:

$$HCl + AgNO_3 \rightarrow AgCl \downarrow + HNO_3.$$
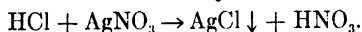
Hydrochloric acid also **interacts** rapidly **with** most **oxides and hydroxides of metals,** as, for example, those of zinc:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O,$$
$$Zn(OH)_2 + 2HCl \rightarrow ZnCl_2 + 2H_2O.$$
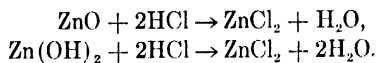
Here no free hydrogen is obtained, since the oxygen in the oxide, and the hydroxyl in the hydroxide, unite with it to form water. In each case, however, the chloride of the metal is obtained.   It may be noted, in passing, that all acids behave in a similar manner towards oxides and hydroxides of metals, giving water and a compound corresponding to the chloride.   Dilute sulphuric acid, for example, gives sulphates.

Uses of Hydrochloric Acid. — This substance is used mainly as a source of chlorine.   It is also employed for cleaning metals and in the manufacture of chlorides of metals.   Although present in very small proportions (about 1 part in 500) in the gastric

juice of the stomach, it is a most important component of this fluid. It is sometimes given as a medicine, when the natural supply is too small.

Double Decomposition. — In this chapter we have met for the first time with **another variety of chemical change.** If we examine the equation for the action of silver nitrate on hydrochloric acid (p. 167), it will appear that the silver nitrate decomposed into its two radicals, namely (Ag) and (NO$_3$). The hydrochloric acid similarly separated into its two radicals (H) and (Cl). The (Ag) then united with the (Cl) and the (H) with the (NO$_3$).

$$(Ag) (NO_3) + (H) (Cl) \rightarrow (Ag) (Cl) + (H) (NO_3).$$
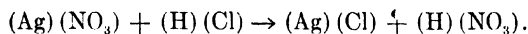
Since both original substances decomposed, this whole change is called a **double decomposition.** It consists of a simple exchange of radicals of the two substances concerned.

The hydrogen chloride was prepared by an action (p. 162) which, if we write it as follows, is seen to be of the same class:

$$(Na) (Cl) + (H) (HSO_4) \rightarrow (H) (Cl) + (Na) (HSO_4).$$
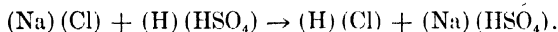
The Varieties of Chemical Change. — Almost all chemical changes belong to one or other of the varieties we have already met with and defined (pp. 11, 19, 59) These, along with one example of each, are now placed together:

1. **Combination:** $Zn + S \rightarrow ZnS$.
2. **Decomposition:** $2KClO_3 \rightarrow 2KCl + 3O_2$.
3. **Displacement:** $Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4$.
4. **Double Decomposition:** $AgNO_3 + HCl \rightarrow AgCl + HNO_3$.

In the first, *2 substances give 1 substance.*
In the second, *1 substance gives 2 (or more) substances.*
In the third, *1 element* and *1 compound give 1 element* and *1 compound.*
In the fourth, *2 compounds give 2 compounds.*

This classification suffices for most purposes. But, for special kinds of cases, some other names are used. Thus, a **dissociation**

p. 83) is an action which belongs to *both* of the first two classes, because it is *reversible*. For example,

$$2H_2O \rightleftarrows 2H_2 + O_2.$$

Electrolysis is decomposition by means of an electric current.

Again **oxidation** (p. 40) and **reduction** (p. 68) are connected with the particular substances, such as oxygen, which are concerned in the action. The foregoing classification pays no atten- · tion to the kinds of elements which are present. Thus, every decomposition is a decomposition. If it is reversible, then it is *also* a dissociation. If oxygen is set free, then it is a reduction *as well.*

SODIUM HYDROXIDE

Preparation of Sodium Hydroxide NaOH from Salt. — The greater-part of sodium hydroxide employed in chemical industries is manufactured by the electrolysis of sodium chloride in concentrated aqueous solution, the other product, chlorine, being of great commercial value also.

• In the electrolysis of hydrochloric acid (p. 65), the hydrogen is set free at the negative wire (cathode). With a solution of sodium chloride we might expect to get free sodium at this wire. It will be recalled, however, that sodium is very much more active than is hydrogen, and indeed displaces hydrogen from water. Hence the electrical energy *sets free the more easily liberated element* — the hydrogen — and the sodium remains in the solution as sodium hydroxide (NaOH). The process is best shown by a diagram:

$$(\text{neg. wire}) \uparrow H_2 \leftarrow 2H \quad \begin{vmatrix} 2Na \\ OH \end{vmatrix} \quad Cl \rightarrow Cl_2 \uparrow (\text{pos. wire})$$
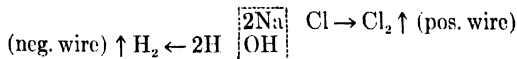
The chlorine Cl_2 and hydrogen H_2, being liberated, leave behind in the solution the constituents of $2NaOH$:

$$2NaCl + 2H_2O + \text{Electrical energy} \rightarrow H_2 + Cl_2 + 2NaOH.$$
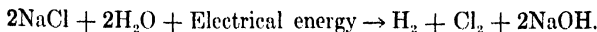
The Nelson cell (Fig. 58) is now most extensively used in commercial practice. A porous diaphragm of asbestos separates the

perforated steel cathode from the carbon anode, which is immersed in a current of brine flowing through the cell between the electrodes. Chlorine is liberated at the anode and rises in bubbles to the surface of the solution. It is drawn 'off, dried, and compressed to liquid form in iron cylinders, or is made directly into bleaching compounds (p. 296). Sodium, as we have seen above, remains in the solution as sodium hydroxide, which collects around the cathode and flows out into a catch basin. It is purified from residual sodium chloride by fractional crystallization. Hydrogen is also liberated at the cathode, and is a valuable by-product of the process.

Copper Bus Bar

Cl₂

Carbon Anode

Slate

Copper Terminal at End of Cell

Perforated Steel Cathode

Asbestos Diaphragm

Steel Tank

Brine

Catch Basin

Caustic Solution
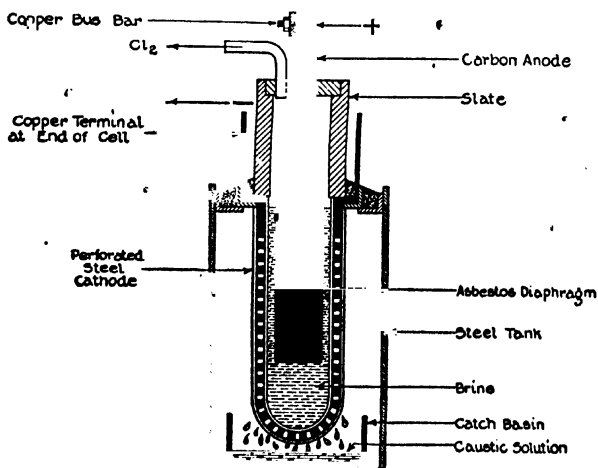
FIG. 58.

Physical Properties of Sodium Hydroxide. — The substance is a *white* crystalline solid. Generally it shows the form of the iron drums, into which it is run when melted, or of the sticks into which it is cast. It is exceedingly *soluble* in water. Its solution gives to objects the smooth, *soapy feeling* which is characteristic of alkalies. The solution is sometimes called **soda-lye,** and the solid, **caustic soda.**

Chemical Properties. — Sodium hydroxide is exceedingly *stable*, being melted, but not decomposed, by heating.

The *aqueous solution* possesses the following important properties. (1) The solution has *an acrid taste*, like soap or borax. (2) It *changes the color of litmus*, reddened by a trace of an acid, back again from red to blue. (3) It is a *conductor of electricity*, and is decomposed by the current, *oxygen being liberated* at the positive wire.

In a following chapter we shall see that these three properties of sodium hydroxide in aqueous solution are properties common to *all substances called alkalies*. The reader should at this point refer back to p. 167, and contrast these properties with those exhibited by *acids*.

Sodium hydroxide in solution *enters into double decomposition* with many substances. Frequently one of the products is insoluble, and appears as a precipitate. For example, with a solution of cupric chloride, sodium hydroxide gives a precipitate of cupric hydroxide.

Skeleton: $\quad$ $NaOH + CuCl_2 \rightarrow Cu(OH)_2 \downarrow + NaCl.$
Balanced: $\quad$ $2NaOH + CuCl_2 \rightarrow Cu(OH)_2 \downarrow + 2NaCl.$

As this equation shows, sodium hydroxide behaves in such actions as if it is decomposed into its two radicals, namely (Na) and (OH) (compare p. 168). The reaction appears to consist, essentially, of a transfer of (OH) radicals from (Na) to (Cu), and of (Cl) radicals from (Cu) to (Na).

Sodium hydroxide, in aqueous solution, also interacts with acids, as, for example, hydrochloric acid (compare p. 167) or sulphuric acid.

$$NaOH + HCl \rightarrow NaCl + H_2O.$$
$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O.$$
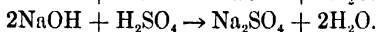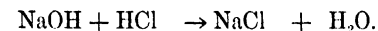
Alkalies and Bases. — It will be seen that the chemical properties of sodium hydroxide solution may be summed up by saying that it is an **alkali**.

Solutions of the alkalies also *act upon animal matter, e.g.*, wool (p. 551), especially when hot, converting it largely into soluble substances. For this reason they are called *caustic* alkalies

They likewise act slowly upon the components of glass. For this reason a precipitate is often visible in the caustic soda reagent bottle, and the inner surface of the glass is always etched.

A very delicate **test** for an alkali is given by *phenolphthalein,* a colorless organic substance. One drop of phenolphtkalein solution added to an alkali in water solution produces an intense *red* (when dilute, *pink*) coloration. Addition of excess acid renders the solution colorless again.

' The alkalies, however, are simply the more active members of a much larger class of substances called **bases.** Solutions of the less soluble bases, of which cupric hydroxide is an extreme example, do not show, distinctly, all the properties exhibited by alkalies. Thus, those which are least soluble have, naturally, no taste, do not visibly affect litmus, do not conduct the electric current very well in solution, and are not soapy to the touch or corrosive towards glass. But they all show the tendency to double decomposition, in which the group (OH) is transferred, as it was from NaOH to $Cu(OH)_2$ in the foregoing example.

Uses of Sodium Hydroxide. — Sodium hydroxide is used in immense quantities along with fats, in the manufacture of soap. Some bleaching liquids are made by saturating it with chlorine. It is employed also in making many other sodium compounds which are used in the arts.

Exercises. — 1. Complete the equation $ZnCl_2 + H_2SO_4 \rightarrow ZnSO_4 +$, and attach the name of the substance to each formula in it.

2. Point out the differences in physical properties between oxygen and hydrogen chloride.

3. Give additional examples of the four varieties of chemical change (p. 168).

4. Classify (p. 168) the following actions: (a) the action of steam on iron (p. 60); (b) the rusting of iron; (c) the electrolysis of dilute hydrochloric acid (p. 65); (d) the effect of heating the hydrate of cupric sulphate (p. 84).

5. What weight of hydrogen is displaced by the action of 100 g. of zinc upon an excess of hydrochloric acid?

6. What weight of silver chloride is formed by the interaction of 5 g. of silver nitrate with excess of hydrochloric acid?

7. What weight of cupric hydroxide is formed by the interaction of 10 g. of blue-stone ($CuSO_4,5H_2O$) with excess of sodium hydroxide in aqueous solution?

8. What different modes of preparing chlorides have been mentioned in this chapter? Write the equation in each case.

CHAPTER XIII

CHLORINE

CHLORINE was first recognized as a distinct substance by Scheele (1774). He obtained it from salt by means of manganese dioxide, using the method described below. It was supposed to be a compound containing oxygen until Davy (1809-1818) demonstrated that it was an element.

Occurrence. — Chlorine does not occur free in nature. There are, however, many compounds of it to be found in the mineral kingdom. Sea-water contains a number of chlorides in solution. Of the 3.6 per cent of solid matter in sea-water, nearly 2.8% is sodium chloride NaCl. During past geological ages the evaporation of sea-water has led to the formation of immense deposits of the compounds usually found in such water. Thus, at Stassfurt, such strata attain a thickness of over a thousand feet. Certain layers of these strata are composed mainly of sodium chloride (rock salt). In other layers potassium chloride (sylvite), an indispensable fertilizer, and other compounds of chlorine occur.

Preparation. — Chlorine cannot be obtained with the same ease as oxygen. There are only a few chlorides, such as those of gold and platinum, which lose chlorine when heated, and they are too expensive or difficult to make for laboratory use. We employ therefore methods like those used for the preparation of hydrogen (compare p. 59). We may (1) decompose any chloride by means of electricity, just as, to get hydrogen, we electrolyzed a dilute acid (p. 65). Or (2) we may take some inexpensive compound of chlorine, such as hydrogen chloride (HCl), and by means of some simple substance which is capable of uniting with the other constituent — here oxygen serves the purpose — secure the liberation of the element. Or (3) — and this turns out to be the most convenient laboratory method — we may use a more complex action.

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Electrolysis of Chlorides. — Hydrogen chloride and those chlorides of metals which are soluble in water are all decomposed when a current of electricity is passed through the aqueous solution yielding chlorine at the positive electrode (see pp. 66, 169). Since the chlorine is soluble in water, the effervescence due to its release is not noticeable until the liquid round the electrode has become saturated with the gas: Cl_2 (dissolved) $\rightleftarrows Cl_2$ (gas). The shape of the apparatus (Fig. 59) keeps the two products from mingling. The presence of the chlorine in the liquid at the positive end may be shown by a suitable test (p. 181).
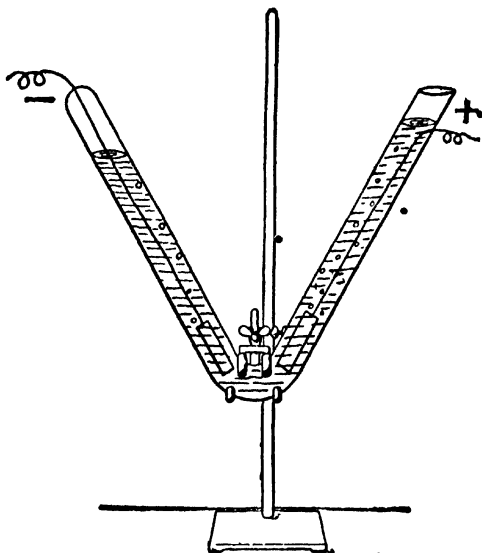
FIG. 59.

In commerce chlorine is now obtained chiefly by this method, sodium chloride or potassium chloride being the source of the element. The apparatus employed and the practical details of the process have already been described in connection with the manufacture of sodium hydroxide (p. 170).

**Preparation of Chlorine from Oxygen and Hydrogen Chlo-
ride.** — When hydrogen chloride and oxygen gases are heated,
they interact very slowly to give water and chlorine. The action
is greatly hastened by contact with copper chloride. Lumps of
pumice, saturated with a so-
lution of this catalyst (see p.
33), are placed in a tube.
When the mixture of gases is
passed over the heated pumice (Fig. 60), steam, chlorine, and,
about 20 per cent of unchanged oxygen and hydrogen chloride
issue at the other end:
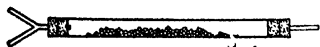
Fig. 60.

Skeleton equation: $HCl + O_2 \rightleftarrows H_2O + Cl_2$.
Balanced equation: $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$.

Longer heating does not alter the proportion of the materials
successfully transformed. This is **Deacon's process.**

That 80 per cent is changed, and 20 per cent unchanged, is
due to the fact that the action is *reversible.* If we lead pure
chlorine and steam through the tube (read the equation back-
wards), 20 per cent of hydrogen chloride and oxygen are formed.
No more than 20 per cent is formed, because these products are
continually being used up again and reproduce steam and
chlorine. If one product could be separated (p. 164) from the
other, to prevent the backward action, the yield could be raised
to 100 per cent. But all the four substances are gases (in the
hot tube), and mix perfectly.

The results here noted are interesting, because they show that,
under the conditions of the experiment, oxygen is somewhat more
active than chlorine in combining with hydrogen. The precise
proportions of the four gases present at equilibrium depend on
the temperature at which the experiment is carried out. In the
commercial application of Deacon's process, this is near 345°.

**Preparation of Chlorine from Hydrochloric Acid and an
Oxidizing Agent.** — The best way to make a supply of chlorine
in the laboratory is to place potassium permanganate crystals
($KMnO_4$) in a flask (Fig. 61) and allow concentrated hydro-

chloric acid, previously mixed with an equal volume of water, to fall upon them drop by drop. The gas is rather soluble in water, and is best collected by displacing the air from bottles. When one bottle is full, it is stoppered and a fresh one substituted. To avoid the escape of the very irritating gas into the room the tube from the collecting bottle dips beneath sodium hydroxide solution, by which the gas is readily absorbed.
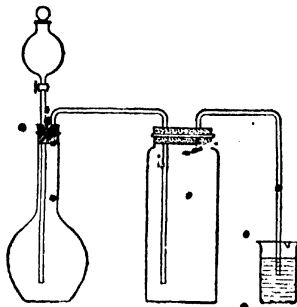
The essential feature of this reaction is that the oxygen of the potassium permanganate unites with the hydrogen of the hydrochloric acid to give water. The potassium and manganese take as much chlorine as they require to form their chlorides, KCl and $MnCl_2$. The rest of the chlorine is liberated.

Skeleton: $KMnO_4 + HCl \rightarrow H_2O + KCl + MnCl_2 + Cl_2$.

To convert all the oxygen of the $KMnO_4$ to water, we require 8HCl. The formation of KCl and $MnCl_2$ uses up 3 of the 8 atoms of chlorine thereby made available, leaving 5Cl to be liberated. Since this chlorine is obtained as Cl_2, it is necessary to *double* our quantities throughout.

Balanced: $2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2$.

This action is an *oxidation of the hydrogen chloride* by the permanganate. The potassium permanganate, which supplied the oxygen, is called the *oxidizing agent*. Since the permanganate lost oxygen, it was itself *reduced*. In all oxidations one substance is oxidized and another reduced.

Deacon's process (p. 176) is also an oxidation of hydrogen chloride (by free oxygen). The oxygen is reduced to water.

Other Means of Oxidizing Hydrogen Chloride.— Many other compounds of oxygen with metals interact with hydro-

FIG. 61.

chloric acid to give free chlorine. Lead dioxide PbO₂, potassium dichromate K₂Cr₂O₇, and manganese dioxide MnO₂, are of this nature. The last, being inexpensive, is commonly used in making chlorine. Being an almost insoluble substance, however, the manganese dioxide acts much more slowly than does the potassium permanganate, which is readily soluble. A large amount of the materials, and the aid of heat, are required to secure a rapid stream of chlorine.

Manganese Dioxide and Hydrogen Chloride. — The action of manganese dioxide upon hydrochloric acid is an instructive one. It is a **general rule**, of which we shall meet many applications, **that when an acid interacts with an oxide of a metal,** there are two constant features in the result, namely: (1) **The oxygen of the oxide combines with the hydrogen of the acid to form water, and (2) the metal of the oxide combines with the acid radical of the acid** (compare p. 167). Here the skeleton equation should be $MnO_2 + HCl \rightarrow H_2O + MnCl_4$. With O_2, to form water, $4HCl$ is required, and the product is $2H_2O$. Hence the equation is

Balanced: $MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_4.$
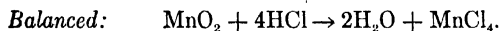
This is, undoubtedly, what happens in the first place. The products actually obtained on heating the mixture, however, are water, manganous chloride $MnCl_2$ and chlorine. We owe the chlorine to the fact that the tetrachloride is unstable. At low temperatures it decomposes into manganese trichloride ($MnCl_3$) and chlorine. When the mixture is warmed, the $MnCl_3$ breaks down further into $MnCl_2$ and chlorine. The complete series of reactions may be represented in one equation as follows:

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2. \qquad (1)$$
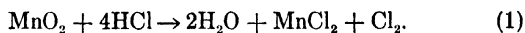
If we had used *manganous oxide* MnO, we should have had a double decomposition:

$$MnO + 2HCl \rightarrow H_2O + MnCl_2, \qquad (2)$$
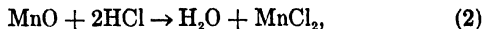
but we should obtain no chlorine. Perhaps the simplest way to describe the difference between these two actions is in terms of

the valence of the manganese. In $Mn^{IV}O_2^{II}$ the element is quad-rivalent. This means that its atomic weight professes to be able to hold four atomic weights of a univalent element. The four valences of oxygen ($2O^{II}$) can do the same thing. In equation (1) the oxygen fulfils this promise by taking $4H^I$. But the Mn^{IV} can hold only $2Cl^I$, permanently, and lets the other $2Cl^I$ go free. In other words, the *valence* of the atomic weight of *manganese changes* in the course of the action. In equation (2), on the other hand, the manganese is bivalent to start with ($Mn^{II}O^{II}$), and is able to retain the amount of chlorine ($2Cl^I$) equivalent to O^{II}. Actions like that of manganese dioxide in (1) are classed as oxidations. The hydrogen chloride, or rather half of it, is oxidized. A graphic mode of writing may make this remark clearer:

$$Mn^{IV} \underset{\diagdown}{\overset{\diagup}{}} \begin{array}{l} O + 2HCl \rightarrow H_2O + Mn^{II}Cl_2 \\ O + 2HCl \rightarrow H_2O + Cl_2 \end{array}$$
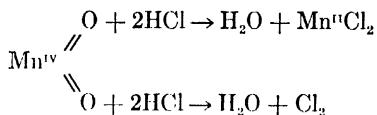
The upper half is a double decomposition, the lower an oxidation by half the combined oxygen of the dioxide. The same explanation applies to the interaction of lead dioxide with hydrochloric acid.

Physical Properties. — Chlorine is a *greenish-yellow* gas, and takes its name from the Greek word for this color. It has an exceedingly disagreeable *odor* and irritates the lining of the nose and throat. Alcohol vapor or ammonia, when breathed, relieves the irritation.

The *density* of the gas is recorded in the formula Cl_2. The 22.4-liter-cube-full weighs 70.92 g., against 28.95 g. for air, so that chlorine is about 2½ times heavier. 215 volumes of the gas *dissolve* in 100 volumes of water at 20°. The solution is called **chlorine-water.**

The gas may be *liquefied* by pressure below 146° (its critical temperature), the pressure required at 20° being 6.6 atmospheres. The liquid boils at −33°, and solidifies at −102° to give a pale-yellow solid. Liquid chlorine was first obtained by Northmore (1806).

Chemical Properties. — *Chlorine is an element with about the same degree of activity as oxygen (compare p. 176), and it unites with very much the same list of other elements. The binary compounds formed are called chlorides.*

Unites with Metals. — When powdered antimony (cold) or iron powder (warmed) are thrown into chlorine, they combine with it, and red hot particles of the chlorides, $SbCl_3$ or $FeCl_3$, fall to the bottom. Copper leaf (Dutch metal, used in "gilding"), or heated copper foil, *burns* in the gas, giving a fog of solid cupric chloride $CuCl_2$.

Skeleton: $Sb + Cl_2 \rightarrow SbCl_{3,}$
Balanced: $2Sb + 3Cl_2 \rightarrow 2SbCl_3.$
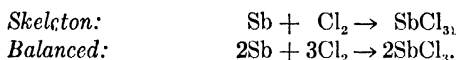
Sodium burns brilliantly in chlorine, giving sodium chloride. That a shining metal and a poisonous irritant like chlorine, in uniting, should yield a mild, household article like common salt illustrates very well the extraordinary nature of chemical change.

When thoroughly freed from moisture, chlorine no longer combines with metals like copper and iron. *Water* seems to be needed as a *contact agent*, in these, as well as in hundreds of other chemical actions. Hence, carefully dried chlorine in compressed liquid form can be, and is, stored and sold in iron cylinders (see detinning, p. 636).

Unites with Hydrogen. — A jet of burning hydrogen, lowered into a bottle of chlorine, continues to burn, giving hydrogen chloride HCl, the presence of which is shown by the fog produced by allowing the gas to come in contact with moist air:

$$H_2 + Cl_2 \rightarrow 2HCl.$$
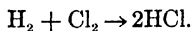
Hydrogen and chlorine, mixed, do not combine when cold, provided strong light is excluded. But sunlight, or light from burning magnesium ("flashlight powder"), starts the combination, which occurs with explosive violence. Plunging a lighted taper into the mixture has, of course, the same effect.

Acts upon Compounds Containing Hydrogen. — Because of its activity toward hydrogen, chlorine removes hydrogen from many compounds. Thus, if a lighted wax taper be plunged into chlorine, it continues to burn, though with a feebler flame. Dense smoke, composed of particles of free carbon, rises from the flame. Blowing the breath into the jar, afterwards, gives the fog due to hydrogen chloride. Thus the presence of hydrogen and carbon in the wax of the taper is proved. From this we learn, also, that chlorine has a relatively small tendency to combine with carbon. A few drops of warm *turpentine* ($C_{10}H_{16}$) upon a slip of filter paper will blaze up in chlorine, giving hydrogen chloride and an immense cloud of soot (finely-divided carbon):

Skeleton: $\quad C_{10}H_{16} + Cl_2 \rightarrow \quad C + \quad HCl.$

Balanced: $\quad C_{10}H_{16} + 8Cl_2 \rightarrow 10C + 16HCl.$
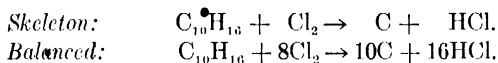
Elements Displaced by Chlorine. — The action on turpentine is a displacement of the carbon by the chlorine. Of the same nature is the action of chlorine upon potassium iodide KI, dry or in solution.

$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$
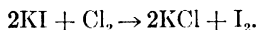
The iodine, when moist, is deep brown in color. A mere trace of chlorine, liberating a trace of iodine, gives no visible effect. But if some starch is present, even a trace of free iodine yields a deep blue color. This reaction is used as a test for chlorine, for free iodine from any source, and for starch (p. 5). To test for chlorine, strips of filter paper, dipped in starch emulsion (starch boiled with much water and cooled) to which a few drops of potassium iodide have been added, are used. *Combined* iodine, as in potassium iodide, has no effect upon starch. Combined chlorine, as in sodium chloride, has no action upon the prepared strips of paper — free chlorine is required.

Action upon Water. — We have seen that chlorine seizes the hydrogen in turpentine. We have also learned that it combines with the hydrogen in steam, reversing Deacon's process to the extent of 20 per cent. It also acts upon **cold water,** when dissolved

in the latter, although in a similarly incomplete way. The substances formed are hydrochloric acid and **hypochlorous acid** HOCl:

$$H_2O + Cl_2 \rightleftharpoons HCl + HOCl.$$
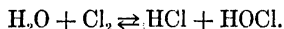
With half-saturated chlorine-water at 10° — that is, water containing about an equal volume of chlorine gas (see p. 179) — about one-third of the chlorine is changed into the acids. Thus, chlorine-water (the solution) is a mixture containing dissolved chlorine and two acids. Hypochlorous acid (see p. 294) is of especial interest because it is a very active substance, with powerful oxidizing qualities, and bleaches dyes by decomposing them.

The action comes to a standstill when one-third completed, because the two acids interact to reproduce chlorine and water (read the equation backwards). The action is thus *reversible*. When the solution is exposed to sunlight, the hypochlorous acid decomposes and oxygen gas is liberated and escapes:

$$2HOCl \rightarrow 2HCl + O_2 \uparrow.$$

Since this removes the hypochlorous acid, on whose interaction with the hydrogen chloride the reverse action depends, the forward action *proceeds under continuous illumination* gradually *to completion*. Hence an aqueous solution of chlorine must be kept in the dark, since otherwise, after a time, a dilute solution of hydrogen chloride alone remains.

The reader should note here the displacement of the equilibrium, a chemical one in this case, in consequence of the annulment of one of the opposing tendencies (p. 86). Through the destruction of the hypochlorous acid, one of the tendencies, namely that represented in the backward action, becomes inoperative. The forward action is not itself assisted, but it is no longer impeded, and so proceeds to completion.

Action by Substitution. — When actions like that on turpentine — that is on compounds containing carbon and hydrogen — are moderated by altering the conditions, the decomposition is not so complete. Using a lower temperature is effective. Thus,

if methane CH_4 (marsh-gas), the chief component of natural gas, is mixed with chlorine and exposed to sunlight, a slower action occurs, of which the first stage consists in the removal of one unit weight of hydrogen and the **substitution** of chlorine for it according to the following equation,

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$
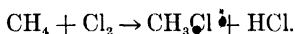
The process may continue further by the substitution of chlorine for the units of hydrogen one by one until carbon tetrachloride CCl_4 is finally formed.

Substitution resembles displacement (p. 59) in that an element and a compound interact, and the element takes the place of one unit in the composition of the latter. In the above action, one unit of chlorine takes the place of one unit of hydrogen. But *the latter is not liberated;* it combines with another unit of chlorine. The action resembles double decomposition, excepting that one of the substances is not a compound, but a diatomic element. The name used is intended to fix the attention on the *compound* and on the fact that one unit has been *substituted* for another in it. This conception is a favorite one in the chemistry of compounds of carbon.

Combines with Non-Metals. — Phosphorus burns in chlorine with a rather feeble light, producing primarily phosphorus trichloride PCl_3, a liquid (b. p. 74°). If excess of chlorine is present, then, as the trichloride cools, it combines to form the solid pentachloride PCl_5 (see p. 121). Sulphur, when heated, unites more slowly, giving sulphur monochloride S_2Cl_2, a liquid used in vulcanizing rubber. Chlorine does not combine directly with carbon, nitrogen, or oxygen, although compounds with those elements can be made indirectly. With the helium group of elements (see p. 376), it forms no compounds.

Combines with Compounds. — Chlorine unites with many compounds. Thus, one of the oxides of carbon, carbon monoxide CO, when mixed with chlorine and exposed to sunlight gives drops of a volatile liquid (b. p. 8.2°) known as **phosgene** $COCl_2$.

When chlorine-water is cooled with ice, a compound, chlorine

hydrate $Cl_2,8H_2O$ crystallizes out. Faraday (1823) placed this substance in the closed limb of a Λ-tube, sealed the open end, and placed the empty limb in cold water (Fig. 62). When the hydrate was gently warmed, chlorine gas was given off and was liquefied by its own pressure in the cold part of the tube.
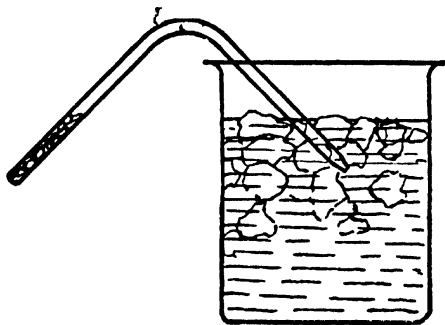
FIG. 62.

Chemical Relations of the Element. * — In the chlorides, an atomic weight of chlorine is equivalent to one atomic weight of hydrogen or of sodium. The element is, therefore, **univalent** (p. 128). It never shows any higher valence than this, save in its oxygen compounds (see Chapter XXI). The oxides of chlorine interact with water to give acids, and the element is, therefore, to be classed as a **non-metal** (p. 83). It belongs to that **group** of the non-metals called the **halogens**, as a consideration of some others of its relations will show (see Chapter XIX).

Uses of Chlorine. — Large quantities of chlorine are manufactured for the preparation of bleaching materials and disinfect-

* In accordance with the distinction that must be drawn (p. 21) between the element as a variety of matter *in combination*, and the elementary substance or free form of the element, and to avoid a common source of confusion, we shall always give only the behavior of the elementary *substance* under the title *chemical properties*. The characteristics which distinguish the *compounds* of the element as a class from, or relate them as a class to, the compounds of other elements will then appear in a separate section under the title "Chemical relations."

ing agents. In disinfection, the minute germs of disease and putrefaction are acted upon either by the chlorine or by the hypochlorous acid formed by its interaction with water, and instantly their life is destroyed.

Chlorine is also a substance of great technical importance in connection with the manufacture of certain explosives and dye-stuffs. For the use of chlorine and of compounds containing chlorine in gas warfare, see Chapter XLII.

Chlorides. — The chlorides are described individually under the other element which each contains. The majority of the chlorides of the metals are easily soluble in water. The chief exceptions are silver chloride AgCl, mercurous chloride (calomel) HgCl, cuprous chloride CuCl, and lead chloride $PbCl_2$. The last of these is on the border line as regards solubility. An appreciable amount dissolves in cold water, and a considerable amount in boiling water (see Table of Solubilities, inside the cover at the front of this book). Various modes of preparing chlorides have been indicated in the previous chapter.

Composition of Hydrogen Chloride. — Now that we are familiar with the properties of chlorine, as well as with those of hydrogen, we may return to the question of the proportion by volume in which they are produced by decomposition of hydrogen chloride. When we electrolyze concentrated hydrochloric acid in the apparatus shown in Fig. 33 (p. 65), we find that the chlorine dissolves to a large extent in the liquid, and its true volume as gas

FIG. 63.

is not easily ascertained. The apparatus (Brownlee's) in Fig. 63 avoids the difficulty by enabling us to saturate the liquid with
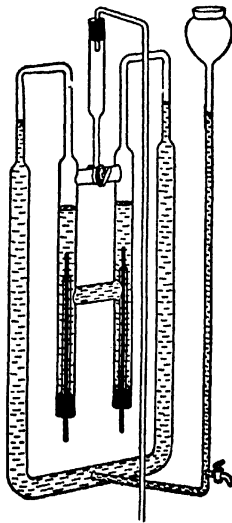
chlorine before observing the collected gases. *The volumes of the two gases are* found to be *equal.*
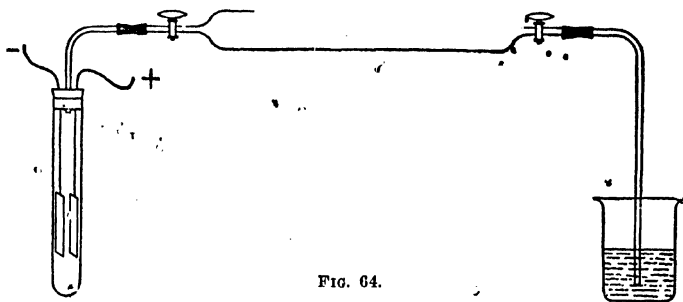
FIG. 64.

A simpler apparatus (Fig. 64) may be used to show the same fact. The gases are generated, by electrolysis of concentrated hydrochloric acid, in the test-tube, pass 'through the straight tube, driving the air before them, and finally bubble through sodium hydroxide solution. The whole apparatus must be covered with a dark cloth to exclude light, and handled in diffused light. In fifteen minutes or so, chlorine ceases to be dissolved in the liquid in the test-tube, and the gases come off in their natural proportions. In half an hour more they have filled the tube. The stopcocks are now closed, the tube is set in a tall cylinder containing potassium iodide (KI) solution (Fig. 65) and the lower stop-cock is opened. The potassium iodide acts upon the chlorine (p. 181), giving potassium chloride and free iodine, and the liquid rises until it *fills half the tube.* The remaining gas, on examination, is found to be pure hydrogen.
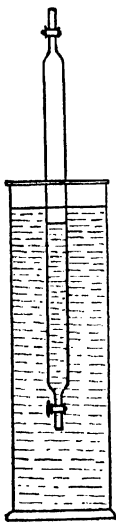
FIG. 65.

The volume of the hydrogen chloride, in relation to the volumes of the constituents, may be learned by using a different apparatus (Fig. 66). A test-tube of heavy glass is filled with dry hydrogen chloride and closed with a rubber stopper greased with vaseline. A little

sodium amalgam (solution of sodium in mercury) is introduced, and the stopper instantly replaced. When the contents are shaken for one or two minutes, the sodium combines with the chlorine and the hydrogen is liberated and remains. The mouth of the test-tube is then immersed in a jar of mercury, and the stopper withdrawn. The water rises and fills *half* the tube.

Conclusion. The hydrogen has half the volume of the hydrogen chloride, and the volume of the chlorine is equal to that of the hydrogen. Therefore:
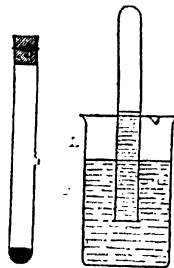
FIG. 66.

1 vol. hydrogen + 1 vol. chlorine → 2 vols. hydrogen chloride.

This result further illustrates Gay-Lussac's law (p. 72).

Confirmation of the Formulæ Cl_2 and H_2. — According to Avogadro's law, there are equal numbers of molecules in equal volumes of these gases. When hydrogen and chlorine combine, one volume of each of these gases gives two volumes of hydrogen chloride. Let us imagine the experiment to be made with minute volumes holding one thousand molecules each:

HYDROGEN		CHLORINE		HYDROGEN	CHLORIDE
1000 mols.	+	1000 mols.	→	1000 mols.	1000 mols.
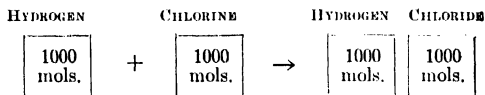
It appears from this that 2000 molecules of hydrogen chloride come from 1000 molecules of hydrogen and 1000 molecules of chlorine. Now, each molecule of hydrogen chloride contains at least one atom of hydrogen, so that the 1000 molecules of hydrogen must have given at least 2000 atoms of hydrogen, one for each molecule of the compound. Hence *each molecule of hydrogen contains at least two atoms.* The same is true of each molecule of chlorine. We have no reason, however, for supposing that there are more than two atoms in either molecule; no substance is known which contains *less than* 1.008 g. hydrogen or 35.46 g. chlorine in its unit weight (p. 94). Hence the con-

clusion is confirmed which we reached before (p. 117), namely, that the formulæ of the free gases are H_2 and Cl_2, and that single atoms of the elements occur only in combination (as in NaCl, HCl, etc.).

CALCULATIONS

Familiarity with the interpretation of **molecular equations** is best obtained by making simple calculations based upon their common uses in chemistry.

Weights. —When a problem in regard to **weights** of material used or produced in a given action is to be solved, the molecular equation is to be written and the weights inserted beneath the formulæ. The mode of calculation has been described already (pp. 123-125).

Weights and Volumes. —When a problem involving **weights and volumes** is to be solved, the molecular equation is to be written, and both the weights and voiumes are to be inserted. Note, however, that only the volumes of the substances *in the gaseous condition* are considered.

For example, what volume of oxygen is obtained from 60 g. of potassium chlorate? The molecular equation, made as already described (p. 112), together with the full interpretation, is as follows:

$$2KClO_3 \quad \rightarrow \quad 2KCl \quad + \quad 3O_2.$$

WEIGHTS: $\left\{ \underbrace{2(39.1 + 35.46 + 48)}_{245.1 \text{ g.}} \quad \underbrace{2(39.1 + 35.46)}_{149.1 \text{ g.}} \quad \frac{3 \times 32}{96 \text{ g.}} \right.$

VOLUMES: $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 3 \times 22.4 \text{ l.}$
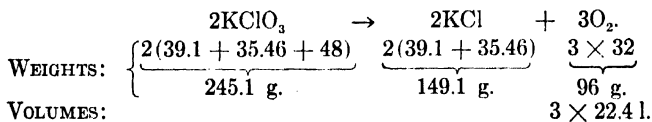
Observe that no volumes are given under the chlorate and chloride of potassium. This is because their volumes in the *gaseous* condition can be of no practical use, since they are solids which are melted, *but not vaporized* during this, or any action in which we employ them. Now, as to the problem in hand, it is concerned with a weight of potassium chlorate and a volume of oxygen. Reading from the equation, our information on *these*

points is that 245.1 g. of potassium chlorate give 67.2 liters of
oxygen at 0° and 760 mm., and the question is: What volume
will 60 g. give? By proportion, 245.1 g. : 60 g. :: 67.2 l. : x l.,
whence $x = 16.45$ liters. If a different temperature and pressure
had been specified, either the volume in the equation, or the an-
swer, would have had to be converted, by rule, to the given con-
ditions.

It saves time not to write out, as above, the whole interpreta-
tion, but only the parts required. For example, if the question
is: What volume of chlorine is needed to give 25 g. of aluminium
chloride? we may, if we choose, omit all the data excepting the
volume of the chlorine and the weight of the aluminium chloride,
thus:

$$2Al + \quad 3Cl_2 \quad \rightarrow \quad 2AlCl_3$$
$$3 \times 22.4 \text{ l.} \qquad 2 \times 133.5 \text{ g.}$$
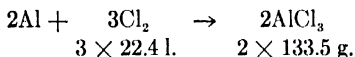
The volume of chlorine required is $25 \times 3 \times 22.4 \div (2 \times 133.5)$
liters.

Relative Volumes Alone. — If the question concerns **relative
volumes** only, then it is simplest to use the interpretation of the
equation in terms of molecules. For example: What relative
volumes of hydrogen chloride and oxygen are required in Deacon's
process (see p. 176)? The molecular equation is

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2.$$
MOLECULES: \qquad 4 \qquad 1 \qquad 2 \qquad 2
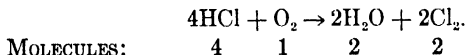
Since equal numbers of molecules of gases occupy equal volumes,
the proportion 4 molecules of hydrogen chloride to 1 molecule of
oxygen shows the ratio to be 4 : 1 by volume. Similarly, every 4
molecules of hydrogen chloride give 2 molecules of chlorine, so
that the ratio of these substances by volume is 4 : 2, or 2 : 1.

In regard to the water, since that is not a gas at common tem-
peratures, the question, if asked, must be more specific: What are
the relative volumes of *steam* and chlorine in the product, as com-
monly delivered by this action at 345°? It is 2 : 2, or 1 : 1.
What are the relative volumes of water and chlorine, after the

products have cooled to room temperature? The water is no longer a gas, so that it occupies, relatively, almost no volume.*

What is the total volume-change in the foregoing action above 100°? It is a change from 5 molecules to 4. The volume changes in the same ratio. But at 0° the volume-change is from 5 volumes to 2, for the water does not appreciably add to the volume of the products.

Relative Volumes, Again. — When we know the molecular formulæ of the single substances concerned in an action, the equation can be made, and **the relative volumes determined, without actual measurement.** For example: What volume-change will be observed when a mixture of carbon monoxide and oxygen has exploded, and the temperature has once more reached that of the room? The molecular formulæ are CO, O_2, and CO_2. The equation representing the reaction, when properly balanced, *must* be written:

$$2CO + O_2 \rightarrow 2CO_2.$$
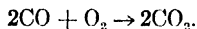
Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two, if the pressure and temperature are the same at the beginning and end of the action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation for any such combustion may easily be made, and the volumes of all the materials ascertained. When water is a product, only its volume as steam is given by the equation.

Relative Densities of Gases. — Knowing by heart the molecular formulæ of gaseous substances, as we must know them for many purposes, it is unnecessary to burden our minds with other data in regard to the **relative weights of gases.** Is hydrogen

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* Of course if an exact answer *must* be given, it can be given. But for this we require the weight and specific gravity of the product. Thus, $2H_2O$ represents 2×18 g. of water. The sp. gr. of water is 1. Therefore the volume of water formed is 36 c.c. The volume of $2Cl_2$ is 2×22.4, or 44.8 liters at 0°. The ratio of water to chlorine by volume at 0° is therefore 36: 44,800. But, as a rule, we simply give the volumes of solids and liquids as *zero*, compared with those of the gases concerned in the same action.

chloride (HCl) heavier or lighter than carbon dioxide (CO_2)?
These formulæ represent the weights of equal volumes (22.4 l.),
namely, 36.468 g. and 44.005 g., respectively. Hence the former
gas is a little lighter.

Remembering that the G.M.V. of air weighs 28.95 g. (p.
134), we can compare the weight of any gas with that of air in
the same way. What are the relative weights of acetylene (C_2H_2,
p. 118) and sulphur dioxide (SO_2) as compared with air? The
G.M.V. cube holds formula-weights of the first two, namely
26.026 g. and 64.06 g., and 28.95 g. of air. Hence acetylene is a
little lighter than air, and sulphur dioxide more than twice as
heavy.

Exercises.—1. What would be the results of electrolyzing
aqueous solutions of: (a) potassium chloride; (b) cupric chloride
(compare p. 64).

2. How should you separate the chlorine and the steam pro-
duced by Deacon's process?

3. Make equations showing the interactions with hydrochloric
acid of: (a) lead dioxide; (b) potassium dichromate. The metals
form $PbCl_2$, KCl, and $CrCl_3$, respectively.

4. What would be the pressure in a cylinder of liquid chlorine
at 20°?

5. Make equations for the union of chlorine with: (a) copper;
(b) sodium; (c) iron; (d) phosphorus; (e) sulphur.

6. When plunged into chlorine, a jet of illuminating gas con-
tinues to burn. A stream of soot rises from the flame, however,
and blowing the breath into the jar, afterwards, produces a fog.
What do you infer as to the constituents of illuminating gas?

7. What information is conveyed by the fact that the formula
of the chloride of sulphur is written S_2Cl_2, and not SCl?

8. Make the molecular equation for the action of sodium upon
hydrogen chloride (p. 187). Why does not the mercury interact
with the latter (compare p. 64)?

9. What facts led us, in Chapter IX, to the conclusion that the
molecular weight of chlorine was 70.92 while its atomic weight
was 35.46?

10. What are the relative densities (p. 48) of: (a) oxygen and

chlorine; (b) hydrogen and hydrogen chloride; (c) hydrogen and air; (d) methane CH_4 and air?

11. What volume of hydrogen chloride at 0° and 760 mm. is obtained by the interaction of 35 g. of sodium chloride, and an excess of sulphuric acid (p. 162)?

12. What weight of zinc is required to make 100 liters of hydrogen, at 10° and 750 mm., by displacement from hydrochloric acid (p. 64)?

13. What are the relative volumes of the factors and of the products in the interaction between: (a) turpentine vapor and chlorine: (b) oxygen and carbon disulphide vapor (giving SO_2 and CO_2)?

14. What are the relative volumes of the products in the decomposition of: (a) mercuric oxide; (b) chlorine monoxide Cl_2O (chlorine and oxygen are formed)?

15. What are the relative volumes of the volatile substances concerned in the action of water vapor on iron (p. 125)?

16. Using the relative volumes in which oxygen and hydrogen combine to form steam, prove that each molecule of free oxygen is composed of at least two atoms (compare p. 120).

17. Calculate the weight of chlorine dissolved by 100 c.c. of water at 20° (p. 179).

18. What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of potassium chlorate?

19. What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into dehydrated rust (Fe_2O_3)?

20. Write out the molecular equations for the interactions of methane and chlorine giving CH_3Cl; and for the burning of phosphorus (vapor) in oxygen (pp. 88, 122). Deduce the volume relations of the initial substances, and of the products, at various temperatures in each case.

21. Write out the molecular equations for the interactions of acetylene and oxygen (p. 190), and of alcohol vapor (b. p. 78°) and oxygen. Deduce the volume relations of the initial substances and of the products at 0° and at 100° in each case.

22. The molecular weight of cyanogen is 52.03. What is its density referred to air, and what the weight of 1 l. at 0° and 760 mm.? It contains 46.08 per cent carbon and 53.92 per cent nitro-

gen. What is the formula of the substance (pp. 112, 118)? Exploded with oxygen it forms carbon dioxide and free nitrogen. What will be the relative volumes of the materials before and after the interaction (p. 189)?

23. What are the relative weights of equal volumes of hydrogen sulphide (H_2S), and hydrogen iodide (HI), compared with air (p. 191)?

CHAPTER XIV

In the description of both chemical and physical changes, the fact that heat was evolved or absorbed has frequently been mentioned. In several instances a current of electricity has been used to produce chemical change. It is now necessary to collect these scattered facts and classify them for future use.

Physical Accompaniments of Chemical Change. — When iron and sulphur combined (p. 18), and when iron burned in oxygen or copper in chlorine, much *heat was developed*. On the other hand, the decomposition of mercuric oxide, as was pointed out (p. 19), owed its continuance to the persistent application of heat and ceased as soon as the source of heat was withdrawn. Here, apparently, *heat was consumed* during the progress of the change, and the chemical action was limited by the amount of heat supplied. The **production or consumption of heat** may, therefore, be a feature of chemical change.

In the burning of iron or magnesium in oxygen, and in the actions of chlorine on copper and turpentine, **light** was also produced. Conversely, silver chloride (p. 622) can be kept any length of time in the dark, but in sunlight it becomes first bluish and then brown, simultaneously giving off chlorine gas and finally leaving only silver as a fine powder. Silver bromide or iodide, in photographic plates, films, and paper, is changed by light in a similar way, liberating the bromine or iodine. It would appear, therefore, that **light may be given out or consumed** in connection with chemical change.

We have seen (p. 65) that a current of **electricity** may be employed to decompose hydrochloric acid and other chlorides,

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and the battery or other source of the current must be kept going or the chemical change stops. The inverse of this is likewise familiar. If we place in dilute sulphuric acid a stick of the metal zinc, we find that hydrogen is given off (Fig. 67), that the zinc goes into solution as zinc sulphate (p. 62), and that a large amount of heat is developed. The presence of small quantities of other metals in the zinc catalyzes this reaction. If impure zinc in fine particles, with much surface, is used, the temperature of the liquid may even rise spontaneously to the boiling-point. This form of the action produces heat. If, however, we attach the same stick of zinc to a copper wire and, having provided a plate of platinum also connected with a wire, immerse the two simultaneously in the acid (Fig. 68), then a galvanometer, with which the wires are connected, shows at once the passage of a current of electricity round the circuit. Exactly
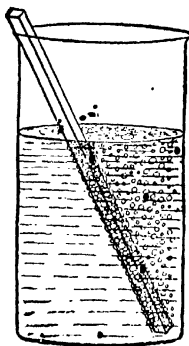
Fig. 67.
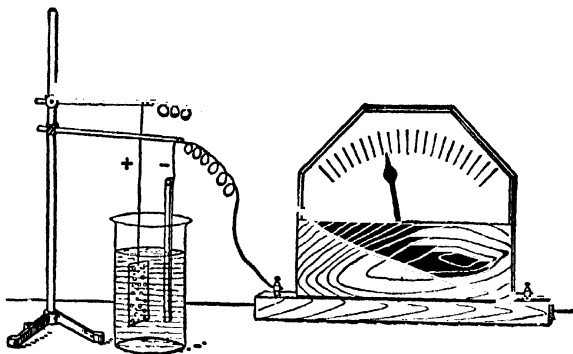
Fig. 68.

the same chemical change goes on as before. The sole difference is that the gas appears to arise from the surface of the platinum. It is easy to show, however, that the platinum by itself is not

acted upon by dilute acids and, in this case, undergoes no change whatever; it serves simply as a suitable conductor for the electricity. Here, then, in place of the heat which the first plan produced, we get an electric current. The arrangement is, in fact, a battery-cell, for a battery is a system in which a chemical action which would otherwise give heat furnishes electricity instead. Thus, **electrical energy may be consumed or produced** in connection with a change in composition.

Even **violent rubbing** in a mortar, in the case of some substances, can effect an appreciable amount of decomposition in a few minutes. In this way silver chloride can be separated into silver and chlorine, just as by light. It is the **mechanical energy** which is the agent, and part of it is *consumed* in producing the change, and only the balance appears as heat. Conversely, the *production* of mechanical energy, as the result of chemical change, is seen in the behavior of explosives and in the working of our muscles. Thus, **mechanical energy may be used up or produced** in chemical changes.

Summing up our experience, we may state that no change in composition occurs without some accompaniments, such as the production or consumption of heat, light, electrical energy, or, in some cases, mechanical energy.

Classification of the Accompaniments of Change in Composition: Energy. — The problem of classifying (*i.e.*, placing in a suitable category) things like heat, light, and electricity has occupied much attention. In all changes in composition, one of these natural accompaniments is given out or absorbed, sometimes in great amount, yet in none is any alteration in weight observed.* There are many things which are real, however, even if they are not affected by gravitation. In the present instance we reason as follows:

A brick in motion is different from a brick at rest. The former can do some things that the latter cannot. Furthermore, we can easily make a distinction in our minds. The brick can be deprived of the motion and be endowed with it again. Thus, we

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* Electrons (see p. 266) do possess mass, but it is quite inappreciable compared with that of the materials concerned.

can get the idea of motion as a separate conception. Similarly, we observe that a piece of iron behaves differently when hot, and when cold, when bearing a current of electricity, and when bearing none. We conceive then of the brick or the iron as having a certain amount and kind of matter which is unalterable, and as having motion, heat, or electricity added to this or removed. Thus, we describe our observations, by using two categories, one of which includes the various kinds of **matter**, and the other, . •various things whose association with matter seems, to be invariable and is often so conspicuous. The latter we call the forms of **energy**.

The Practical Importance of Energy in Chemistry. — The absorption or liberation of energy accompanying a chemical transformation of matter is often, of the two, the more important feature. We do not burn coal in order to manufacture carbon dioxide gas. We are glad to get rid of the material product through the chimney. It is the heat we want. We do not buy gasoline (petrol) for an automobile in order to obtain various gases to expel through the muffler. We really pay for the mechanical energy. It is the same with burning illuminating-gas or magnesium powder when we want light, and with eating food, which we do, chiefly, to get energy to sustain our activity. We do not run electricity for hours into a storage battery, in order to make a particular compound (lead dioxide, for example), but in order to save and store the energy for future use. In industry and life fully half the total amount of chemical change involved is set in motion by us, solely on account of the energy changes it involves. But the production of energy in chemical change is not only thus of practical importance; it is also of scientific interest, as will be seen in the section on energy and chemical activity (see below).

Interconvertibility of Forms of Energy: Conservation. — At first sight, the different forms of energy seem to be quite unrelated. But a relation between them can be found. If the heat of a Bunsen flame or of the sun is brought under a hot-air motor (Fig. 69) violent motion results. Again, if the motor is connected with a dynamo, electricity may be generated. Still

again, if the current from the dynamo flows through an incandescent lamp, heat and light are evolved. Conversely, when motion of the hot-air motor is impeded by a brake," heat appears. When a current of electricity is run through the dynamo, the armature of the latter turns and motion results. But the most significant facts are still to be mentioned. The heat absorbed by the motor is found to be greater when the machine is permitted to move and do work, than when it is not. Thus, it is found that when work is done some heat disappears, and this heat is, in fact, transformed into work. Similarly, when' the poles of the dynamo are properly connected and electricity is being produced, and only then, motion is used up. This is shown by the effort required to turn the armature under these circumstances, and the ease with which it is turned when the circuit is open. So, with a conductor like the filament in the lamp, unless it offers resistance to the current and destroys a sufficient amount of electrical energy, it gives out neither light nor heat. Finally, motion gives no heat unless the brake is set, and effort is then demanded to maintain the motion. These experiences lead us to believe that we have here a set of things which are fundamentally of the same kind, for each form can be made from any of the others. We have, therefore, invented the conception of a single thing, of which heat, light, electricity, and motion are forms, and to it we give the name **energy: energy is work and every other thing which can arise from work and be converted into work.**

FIG. 69.

Closer study shows that equal amounts of electrical or mechanical energy always produce equal amounts of heat. No loss is ever observed in the transformations of energy, any more than in the transformations of matter. Hence we have been led to the conclusion that in **a limited system no gain or loss of energy is ever observed.** This brief statement of the results of many experiments is called the law of the **conservation of energy.**

Application of the Conception of Energy in Chemistry. —

At first sight it looks as if the statement that energy is conserved is not applicable in chemistry. Heat and electricity, for example, seem to be produced and consumed, in connection with changes in composition, in a mysterious manner. We trace light in an incandescent lamp back to the electricity, and this in turn to the mechanical energy, and this again to the heat in the engine. But what form of energy gave the heat developed by the combustion of the coal under the boiler, or by the union of iron and sulphur in our first experiment? Since we do not perceive any electricity, light, heat, or motion, in the original materials, and yet wish to create an harmonious system, we are bound to conceive of the iron and the sulphur, and the coal and the air, as containing another form of energy, which we call **internal energy**. Similarly, when heat is used up in decomposing mercuric oxide, or light in decomposing silver chloride, we regard the energy as passing into, and being stored in, the products of decomposition in the form of internal energy.

These conclusions compel us, for the sake of consistency, to think of all our materials as repositories of energy as well as of matter, each of these two constituents being equally real and equally important. A piece of the substance known as "iron" must thus be held to contain so much iron matter and so much internal energy. So ferrous sulphide contains sulphur matter, iron matter, and internal energy. Thus, by a *substance* we mean a distinct species of matter, simple or compound, with its appropriate proportion of internal energy. During the progress of a chemical change, like the union of iron and sulphur, the internal energy of the system also changes. The *total* energy which can thus be made available as the result of a chemical action, and converted (through, say, heat or electrical energy) into work, is called the *free energy* of the reaction.

In the course of this discussion it has become clear that it is **characteristic** of chemical phenomena that, besides a change in the nature of the *matter*, **there is always an alteration in the amount of internal energy in the system. This alteration involves the production of internal energy from, or the transformation of internal energy into some other form of energy.**

Energy and Chemical Activity. — Other things being equal, when the free energy of a reaction is large, the reaction proceeds rapidly; that is to say, a large proportion of the reacting materials are changed in the unit of time. Those reactions in which the change of internal energy is small proceed more slowly. The speed of a chemical change, and the quantity of energy available because of it, are therefore closely related. Now, we are accustomed to speak of materials which, like iron and sulphur, interact rapidly and with liberation of much energy as "chemically active," or as possessing great "chemical affinity" for one another. Thus, **relative chemical activity** or *affinity* may be estimated, (1) by observing the speed of a change, or, in many cases, (2) by measuring the heat developed, or (3) by ascertaining the electromotive force of the current, when the materials are arranged in the form of a battery-cell (see Chapter XLVI). The *order of activity of the metals*, given on p. 64, is best obtained by this third method.

It is evident that the chemical activity or affinity of a given substance will not be the same towards all others. Thus, iron unites much more vigorously with chlorine than with sulphur and, with identical amounts of iron, more heat is liberated in the former case than in the latter. With silver, sodium, and many other substances, iron does not unite at all. One of the tasks of the chemist is to make such comparisons as this. He calls the results the specific chemical properties of the substances in question.

Care must be observed, however, in making comparisons by the above methods. Although it is true that most chemical changes that take place readily *develop* heat, yet at high temperatures compounds can be formed by the direct union of their elements with *absorption* of heat (see, for example, p. 394). Reversible reactions must also be accounted for. In such reactions, one of the chemical changes taking place necessarily absorbs just as much heat as the other develops, yet both have a definite speed under any given conditions, as is shown by the fact that a fixed point of equilibrium is reached. Deacon's process (p. 176) is a good instance. As we shall see in the next chapter, the rela-

tive *concentrations* of the reacting substances, as well as their *affinities*, must be taken into consideration.

The Cause of Chemical Activity or Affinity. — The reader will undoubtedly be inclined to inquire whether we can assign any cause for the tendency which substances have to undergo chemical change. Why do iron and sulphur unite to form ferrous sulphide, while other pairs of elements taken at random will frequently be found to have no effect upon one another under any circumstances? A final answer to this question cannot, of course, be given. As the facts regarding chemical activity or affinity, however, become better known, we may arrive at a stage where a logical *explanation* (see p. 26) can be advanced which, basing itself on these facts, affords a means of classifying them and supplies us with a new and useful hypothesis regarding matter in its various forms (iron, sulphur, etc.) and the energy contained therein. A brief discussion of such a hypothesis will be found in the concluding chapter (pp. 729-732).

The Speed of Chemical Actions: a Means of Measuring Activity. — One means of measuring the relative chemical activities of several substances is to observe the speed with which they undergo the same chemical change. Thus we may compare the activities of the various metals by allowing them separately to interact with hydrochloric acid and collecting and measuring the hydrogen liberated per minute by each. It will be seen, even in the roughest experiment, that magnesium is thus much more active than zinc. The comparison must be made with such precautions, however, as will make it certain that the conditions under which the several metals act are all alike. Thus, in spite of the heat evolved by the action, means must be used, by suitable cooling, to keep the temperature at some fixed point during the experiment, for all actions become more rapid when the temperature rises (p. 11). Again, the pieces of the various metals must be arranged so that equal surfaces are exposed to the acid in each case. It is found that the order in which this comparison places the metals is much the same as that in which they are placed by

a study of other similar actions. A single table, showing the order of activity (p. 64), suffices, therefore, for all purposes.

Thermochemistry. — Chemical changes in which heat is liberated are called **exothermal.** Those in which heat is continuously absorbed (pp. 19, 31) are called **endothermal** changes. Since the activities, or affinities, of two substances (say, two metals) may often be compared by observing the amounts of heat liberated when each combines with a third substance (say, oxygen), it will be instructive now to consider some of the elementary facts of thermochemistry.

The chemical interactions to be studied thermally are arranged so that they may be carried out in a small vessel which can be placed inside another containing water. The whole apparatus is called a **calorimeter** (Greek, *heat-measurer*). The heat developed raises the temperature of this water. Where gases like oxygen are concerned, a closed bulb of platinum forms the inner vessel. The average quantity of heat required to raise one gram of water one degree in temperature between 0° and 100° C. is called a **calorie** (see p. 72).

Thermochemical Equations. — While in physics the unit of quantity is the gram, in chemistry the unit which we select is naturally a gram-atomic weight or a gram-molecular weight of the substance. Thus, the heat of combustion of carbon means the heat produced by combining twelve grams of carbon with thirty-two grams of oxygen, and is sufficient to raise nearly 100,000 grams of water one degree. This is expressed as follows:

$$C + O_2 \rightarrow CO_2 + 96{,}900 \text{ cal.}$$
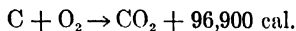
In other words, the combustion of less than half an ounce of carbon will raise over two pounds of water from 0° to the boiling-point.

When the action is one which absorbs heat, this fact is indicated by the negative sign preceding the number of calories. Thus for the dissociation of water vapor into hydrogen and oxygen we have the thermochemical equation:

$$2H_2O \rightarrow 2H_2 + O_2 - 116{,}200 \text{ cal.}$$
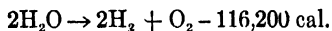
If the action is reversible, as this one is, the heat absorbed when it proceeds in one direction is equal to that liberated when it goes in the other direction:

$$2H_2 + O_2 \rightarrow 2H_2O + 116,200 \text{ cal.}$$
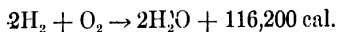
Answers to Possible Questions.—It is always found that the same quantities of any given chemical substances, undergoing the same chemical change under the same conditions, produce or absorb, according as the action is exothermal or endothermal, amounts of heat which are equal.

The *rate* at which a given chemical action is allowed to take place has no influence on the total amount of heat consumed or produced. It may not at first sight appear obvious that rusting evolves heat, but a delicate thermometer will show that a heap of rusting nails is somewhat higher in temperature than surrounding bodies. - Poor conductors, like oily rags and ill-dried hay, show a tendency to spontaneous combustion owing to accumulation of the slowly developing heat of oxidation (p. 42). The warmth of our own bodies is due to the same cause.

—It should be noted that production or absorption of heat is not, in itself, an evidence of chemical action. Physical changes are all likewise accompanied by the same phenomena. Thus, the evaporation of water absorbs heat, and condensation of a vapor and the crystallization of a supercooled liquid liberate heat. The significance of the heat changes involved in the process of *solution* has already been discussed in an earlier chapter (p. 151).

Exercises. — 1. Which form of energy is delivered as such, and paid for as such, in most cities?

2. How many calories are required to raise 500 g. of a substance of specific heat 0.5 from 15° to 37°?

3. The combustion of 1 g. of sulphur to sulphur dioxide develops 2220 calories. What is the heat of combustion of sulphur? Write the thermochemical equation.

CHAPTER XV

IN spite of its formidable title, this chapter will introduce nothing novel. Its purpose is to collect together and organize more definitely a number of scattered facts and ideas which have already come up in various connections. On this account, however, it will be all the more necessary for the reader to refresh his remembrance of these facts and ideas by re-reading all pages to which reference is made.

Reversible Actions. — In discussing Deacon's process (p. 176), it was stated that the action $4HCl + O_2 \rightarrow 2H_2O + 2Cl_2$ comes to rest although a large amount of *both* of the interacting substances (20 per cent at 345°) still remains available. Now the materials thus left unused are presumably no less capable of interacting than were the parts which have already reacted. The solution of this mystery lies in the fact that the *products themselves interact* to reproduce the initial substances (read the equation backwards). Thus two changes, one of which undoes the work of the other, are going on simultaneously. In consequence of this, neither action can reach completion.* As we should expect, experiment shows that it makes no difference whether we *start* with pure chlorine and steam, or with hydrogen chloride and oxygen; the proportions of the four substances found in the tube, after it has been kept at 345° for a sufficient time, are in both cases the same. A **general statement** may be founded on facts like this, to the effect that **a chemical action must remain more or less incomplete when the reverse action also takes place to an appreciable extent under the same conditions.** Two arrows pointing in opposite directions are used in equations representing reversible changes.

* The reader must avoid the idea that a reversible action is one which goes to completion, and then runs back to a certain extent. This conception would be contrary to the fact, and inexplicable by the kinetic method.

The foregoing example of a reversible action, and the following examples which very closely resemble it, should now be looked up and studied attentively. The discussion in this and the following sections, for which they furnish the basis, cannot otherwise be understood: (1) the behavior of water vapor at the boiling-point (pp. 77-79) and at 2000° (p. 82); (2) the depression of the vapor pressure of a liquid by a non-volatile solute (p. 153); (3) the action of *dilute* sulphuric acid on common salt (pp. 163-164); (4) the interaction of chlorine and water (p. 182); (5) the dissociation of phosphorus pentachloride into phosphorus trichloride and chlorine (p. 121).

In many important reversible reactions, the concentrations of the reacting substances on one side of the equation are, under equilibrium conditions, very much greater than the concentrations of those on the other side. Although the reaction is reversible, it proceeds much farther towards completion in one direction than the other. This fact may often be indicated, very conveniently, by modifying the thickness of the arrows used to express reversibility. Thus:

$$2H_2O \rightleftarrows 2H_2 + O_2 \qquad PCl_5 \rightleftarrows PCl_3 + Cl_2$$
$$\text{(at 2000°; see p. 82)} \qquad \text{(at 300°; see p. 122)}$$
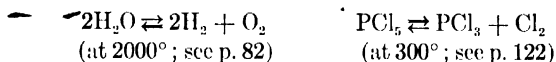
Actions which Proceed to Completion. -- Many chemical reactions do not, apparently, belong to the reversible, incomplete class, but proceed uninterruptedly to exhaustion of one, or all, of the original materials. The decomposition of potassium chlorate by heating (p. 31) is a reaction of this type. Under no known conditions do potassium chloride and oxygen re-combine to form potassium chlorate. In the same way, equivalent amounts of magnesium and oxygen combine completely to form magnesium oxide:

$$2Mg + O_2 \rightarrow 2MgO$$
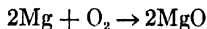
and the product is not decomposed even at the white heat produced by the vigor of the union.

We have a great deal of evidence, however, which points to the conclusion that *all actions are fundamentally reversible,* even although the conditions under which reversibility may be actually

demonstrated are not experimentally available in some cases. Take the case of magnesium oxide cited immediately above. We are familiar with a great many other oxides which, a century ago, had not been directly decomposed into their constituent elements. *Cupric oxide* (p. 38), for example, does not begin to lose oxygen until heated to a temperature approaching 1000°, but in the electric furnace it is completely dissociated. The combination of hydrogen and oxygen to form *water* is complete under ordinary conditions, but partial dissociation at 2000° has now been established (p. 82), while by the utilization of electrical energy (electrolysis) a total reversal of the reaction may be effected at room temperature. Although, therefore, magnesium oxide cannot be decomposed directly at any temperature we can command at present, we are evidently not justified in stating that the reaction written above is inherently irreversible.

In later chapters we shall show that many other reactions which appear to be complete, such as the precipitation of silver chloride (p. 167), the action of an acid on a base (p. 171), and the displacement of hydrogen in an acid by a metal (p. 59), are, *in principle*, truly reversible reactions.

Explanation of a Reversible Reaction in Terms of Molecules.
— Suppose we start with the materials represented on *one side* only of the equation for a reversible reaction, say the hydrogen chloride and oxygen in that on p. 204. The molecules of these materials will encounter one another frequently in the course of their movements. In a certain proportion of these collisions the chemical change will take place. In the earliest stages there will be few of the new kind of molecules (say of chlorine and steam), but, as the action goes on, these will increase in number. There will be two consequences of this. In the first place, the parent materials (in this case hydrogen chloride and oxygen) will diminish in amount, the collisions between their molecules will become fewer, and the speed of the forward action will therefore become less and less. In the second place, the increase in the number of molecules of the products will result in more frequent collisions between them, in more frequent occurrence of the chemical change which they can undergo, and thus in an

increase in the speed of the reverse action. The forward action begins at its maximum and decreases in speed progressively; the reverse action begins at zero and increases in speed. Finally the two speeds *must become equal*, and at that point perceptible change in the condition of the whole must cease.

The most immediate inference from this mode of viewing the matter is, that the apparent halt in the progress of the action does not indicate any cessation of either chemical change. Both changes must go on, in consequence of the continued encounters of the proper molecules. But since the two changes proceed with *equal speeds* they produce no alteration in the mass as a whole. In fact, the final state is one of equilibrium and not of rest, one of balanced activity and not of repose. Hence, chemical changes which are reversible lead to that condition of seemingly suspended action which we speak of as **chemical equilibrium.**

Chemical Equilibrium and its Characteristics. — The detailed discussion of the relations of liquid and vapor (pp. 77-79), and of saturated solution and undissolved solid (pp. 156-157), has already familiarized us with the term equilibrium and its significance. We can, in fact, apply to the discussion of any kind of reversible phenomena the sets of ideas in regard to exchanges of molecules there elaborated.

In particular, the reader will note that the **three characteristics of a state of equilibrium,** developed and illustrated in the case of the physical equilibrium between a liquid and its vapor (pp. 78-79), apply also to a typical case of chemical equilibrium, such as that in Deacon's process now before us. Thus:

1. There are **the two opposing tendencies, which ultimately balance one another.** Here they are the tendency of the steam and chlorine to produce hydrogen chloride and oxygen, and the tendency of the hydrogen chloride and oxygen to reproduce steam and chlorine by this interaction.

2. **At equilibrium the two opposing tendencies or activities are still in full operation,** although their effects then neutralize one another.

3. (This is the chief mark of chemical, as it is of phys-

ical equilibrium). The system is in a sensitive state, so that **a change in the conditions** (temperature and pressure or concentration), even if slight, **produces a corresponding change in the state of the system, and does this by favoring or disfavoring one of the two opposing tendencies or activities.** Such a change is called **a displacement of the equilibrium,** for the system settles down in a new state of equilibrium with new proportions of the two sets of substances, corresponding to the changed conditions. Thus, in the present instance, a change from 345°, where there is 80 per cent of the material in the form of steam and chlorine, to 384° results in the diminution of this proportion to 75 per cent. The equilibrium is affected by changes in concentration also, as we shall presently see.

Now, the foregoing facts show that the key to understanding chemical activities, their magnitudes, their changes, and especially their practical results, *must lie in knowing how changes in the conditions affect them.* Hence, to the chemist, familiarity with the influence of conditions on chemical phenomena must be of the greatest practical importance.

The Influence of Concentration. — In the first place, let us assume that the temperature is constant, and let us confine our attention for the present to the influence of concentration upon a chemical reaction. We have seen (p. 206) that the speed of a chemical change is determined by the frequency with which the molecules of the interacting substances encounter one another. The frequency of the encounters amongst a given set of molecules, resulting in a definite chemical change, will in turn evidently depend entirely upon the degree to which the molecules are concentrated in each other's neighborhood. Larger amounts of one of the materials, for example, will not result in more rapid chemical action, if the larger amount of material is also scattered through a larger space. Chemical changes, therefore, are not accelerated by increasing the mere quantity of any ingredient, but only by increasing the **concentration of its molecules.** Thus, a large amount of a 0.1 normal solution of hydrochloric acid with a piece of zinc will generate hydrogen no faster than a smaller amount. But substitution of a *normal* solution of hydro-

chloric acid will instantly increase the speed of the action. So, also, iron burns faster in oxygen (100 per cent) than in air (20 per cent oxygen).

Similarly, in the action of hydrogen chloride upon oxygen, if we take an equilibrium mixture and introduce *into the same space* an extra amount of *oxygen*, we facilitate the formation of steam and chlorine by increasing the possibilities of encounter between molecules of hydrogen chloride and oxygen. At the same time we do not immediately affect (see p. 47) the number of encounters in a given time of steam and chlorine molecules with one another which result in the reverse transformation. The proportion of chlorine (and steam) formed, therefore, from a given amount of hydrogen chloride will *increase* until a new point of equilibrium is reached, although the total possible (by complete consumption of the materials) has not been altered, since the quantity of one ingredient only has been increased. The introduction of an excess of hydrogen chloride would have had precisely the same effect.

An Experimental Illustration. — A reaction in which the effects of different concentrations were carefully studied by Gladstone (1855) affords a good illustration. If ferric chloride and ammonium thiocyanate are mixed in aqueous solution, a liquid containing the soluble, *blood-red* ferric thiocyanate is produced. The compound radicals are (NH_4) and (CNS), and the action is a simple double decomposition:

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl.$$
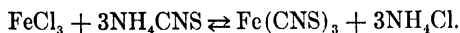
The action is a reversible one, and the mixture is homogeneous, *i.e.*, there is no precipitation. Now, if the two just-named salts are mixed in very dilute solution in the proportions required by the equation, say by adding 20 c.c. of a decinormal solution of each salt to several liters of water, a pale-reddish solution is obtained. When this is divided into four parts, and one is kept for reference, the addition of a little of a concentrated solution of ferric chloride to one jar, and of ammonium thiocyanate to another, will be found to deepen the color by producing more of the ferric thiocyanate. On the other hand, mixing a few drops

of concentrated ammonium chloride solution with the fourth portion will be found to remove the color almost entirely, on account of its influence in favoring the backward change.

The Law of Molecular Concentration. — The general principle discussed and illustrated in this section may be called **the law of molecular concentration,** and may be stated as follows: **In every chemical change the activity, and therefore the speed of the action, is proportional to the molecular concentration of each inter acting substance.** This holds whether the reverse reaction is appreciable or not.

The molecular concentration is expressed, numerically, for each substance, *in terms of the number of moles* (gram-molecular weights, p. 142) *of the substance contained in a liter of the whole mixture.* There is the same number of molecules in a gram-molecular weight of any substance (see p. 91). Hence the number of *moles per liter* defines the concentration of each substance in terms of this number of molecules in a liter as the unit of concentration.

As an example, the dissociation of phosphorus pentachloride vapor into phosphorus trichloride and chlorine (p. 121):

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$
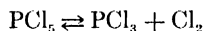
may be considered.

The law states that, in any mixture of the three substances, the speed of the forward action, or decomposition, is proportional to the concentration of PCl_5 molecules. It is therefore *equal* to the concentration of PCl_5 molecules, which we may write $[PCl_5]$, multiplied by a constant, which we shall write K_1. Mathematically expressed, if S_1 is the speed of decomposition:

$$S_1 = K_1 \ [PCl_5]$$

In the same way the law states that the speed of the reverse action, or combination, is proportional to the concentration of PCl_3 molecules and also proportional to the concentration of Cl_2 molecules. It is therefore *equal* to the concentration of PCl_3 molecules $[PCl_3]$, multiplied by the concentration of Cl_2 mole-

cules [Cl_2] multiplied by another constant, which we shall write K_2. If S_2 is the speed of combination, we have now:

$$S_2 = K_2 [PCl_3] \cdot [Cl_2]$$

Each reaction, it will be noted, must slow up as the concentration of the reacting substances diminishes. This is true of all reactions. The further they proceed, the less rapid their speed. The burning of a candle in a confined space becomes less brilliant as the available oxygen is used up. The evolution of hydrogen in the action of an acid on a metal becomes very slow when the acid is nearly exhausted.

The Condition for Chemical Equilibrium. — As we have seen (p. 207), the characteristic of a system in chemical equilibrium is that the speeds of the forward and reverse reactions have become equal. Applying this to the case of the dissociation of phosphorus pentachloride discussed above, we see that, when we have *an equilibrium mixture* of the three substances, where $S_1 = S_2$, then we also have the relationship:

$$K_1 [PCl_5] = K_2 [PCl_3] \cdot [Cl_2]$$

This may be written in the form:

$$\frac{K_1}{K_2} = \frac{[PCl_3] \cdot [Cl_2]}{[PCl_5]}$$

The ratio K_1/K_2 is, of course, a constant, since K_1 and K_2 are both constants. This ratio, which we may write K, is called the **equilibrium constant** of the reversible reaction.

The *equilibrium constant* is a very important quantity. Once we have determined it, by investigating one equilibrium mixture, we can *calculate exactly* what will happen to *any mixture* of the three substances concerned at the same temperature. However much we may vary the molecular concentrations of the three substances, whether by changing the pressure or by adding an excess amount of one of them, such as chlorine, the composition of the mixture will adjust itself until, when equilibrium is attained, the ratio $[PCl_3] \cdot [Cl_2]/[PCl_5]$ has again reached the

value K. In large-scale industrial processes, therefore, a knowledge of the equilibrium constant of the reaction involved is often of inestimable value.

Homogeneous and Inhomogeneous Systems. — While there are all degrees of speed in chemical actions, yet in practice we quickly distinguish two different classes. There is a class of actions of which most examples are almost instantaneously accomplished, and a class in which, frequently, the operation takes minutes or even hours. The classes overlap, but, in a general way, the following distinction may be made.

To the former, speedy class belong the explosion of hydrogen and oxygen or other gaseous mixtures, and the interactions when solutions are mixed, as in precipitations. In view of the foregoing explanations, we perceive that the **rapid accomplishment of** such **actions is due,** not so much to any especially great intrinsic affinity, as **to the homogeneous state of mixture of the interacting materials.** This, of course, is a purely physical, and not a chemical motive for speedy interaction. In intimate mixtures, every molecule has an equal opportunity freely to encounter every other molecule and there is therefore no mechanical impediment to the operation of the affinities of the substances. Hence the apparent activity* is great.

To the second class, comprising the slower actions, belong cases like the interaction of a piece of zinc with hydrochloric acid, or of manganese dioxide (p. 178) with the same acid, whereby hydrogen and chlorine, respectively, are slowly evolved, and the solid is gradually consumed. Here the hindrance is evidently the fact that the interacting substances are not intimately mixed. **In the slow actions, the system is inhomogeneous.** Pulverizing the solid before use will increase the speed, indeed, by providing more surface and better mutual contact, but will not transfer the action to the rapid class. It is chiefly the *dissolved* part of the

* We use the term "apparent activity" for the activity as we see it. In the same action it varies with the conditions. The **intrinsic activity** or **affinity,** on the other hand, is the absolute activity of the action *irrespective of conditions.* Its value can be determined only by eliminating the effect of conditions, a matter which is too abstract for consideration here. The apparent activity is the practical thing which we observe.

substance which interacts, for chemical action takes place be-
tween molecules, and only the dissolved part is disintegrated in
such a way that the molecules are readily accessible. Thus, the
action is held back by continual waiting for the slow replenish-
ment, from the "insoluble" solid, of the supply of dissolved mole-
cules. In the cases cited, the restraining influence of the dissolv-
ing process, which is part of the whole phenomenon, may· be
formulated thus:

$$Zn \text{(solid)} \leftrightarrows Zn \text{ (dissolved)} + 2HCl \rightarrow ZnCl_2 + H_2.$$
$$MnO_2 \text{(solid)} \leftrightarrows MnO_2 \text{(dissolved)} + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2.$$
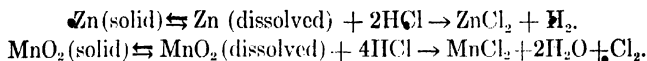
Here, again, the mechanical details, depending on physical prop-
erties, have more to do with the progress of the action than has
the chemical affinity. In terms of the law of concentration, the
action is slow, and the apparent activity small, because the con-
centration of the acting molecules of one of the substances is very
small, and cannot be increased because of low solubility.

Displacement of Equilibria. — We have seen (p. 209) that
one way in which a reversible action may be forced nearer to
completion, in one direction or the other, is the introduction of
an excess of one of the ingredients contributing to the forward
action. This method of displacing the equilibrium point, how-
ever, cannot be very effective, unless it is possible to introduce
an exceedingly large excess of the selected ingredient in a high
degree of molecular concentration, since this operation *does not
in any way affect or, in particular, restrain the reverse action*
which is continually undoing the work of the forward one. A
much more effective **means of furthering the desired direction of
such actions is found**, therefore, **in the restraint or practical annul-
ment of the reverse action.** A good way of accomplishing this is
**to allow the products of the direct action to separate into an in-
homogeneous mixture.** Any agency which could remove the water
vapor as fast as it was formed by the interaction of hydrogen
chloride and oxygen, for example, would entirely stop the re-
production of these substances, and so would enable the forward
action $(4HCl + O_2 \rightarrow 2H_2O + Cl_2)$ to run to *completion.*

This might be realized by causing one end of a sealed tube

charged with the substances, after the contents had settled down to a condition of equilibrium, to project from the bath in which the whole had been kept at 345° (Fig. 70, which is simply dia-grammatic). By cooling this end, a large part of the steam would quickly be condensed in it to the liquid form, while the other sub-stances would remain gaseous. In other words, the concentra-tion of the water vapor would be greatly reduced. In fact, only the trace of vapor which cold water gives would then be avail-able to interact with the chlorine, and reproduce hydrogen chlo-ride. Meanwhile the decomposition of the latter would go on, and thus, eventually, almost all the water would be found in one end of the tube, and the chlorine, all free, would occupy the rest. By this purely mechanical adjustment the chemical change would therefore be carried from 80 per cent completion to almost abso-lute completion:
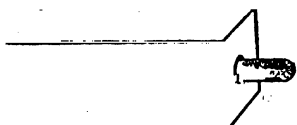
Fig. 70.

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O \text{ (vapor)} \rightleftarrows 2H_2O \text{ (liq.)}$$
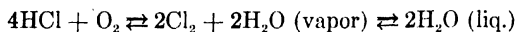
If, on the other hand, arrangements were made to have pow-dered marble, in a sealed bulb of thin glass, enclosed in the tube, we might imagine the very opposite of the above effect to be pro-duced. The breaking of the bulb of marble, when equilibrium had been reached, would provide means for the removal of all the hydrogen chloride,* while the other three substances would still be gaseous. Thus, the hydrogen chloride having been reduced in concentration to the point of being removed entirely, there would be no direct action to undo the work of the reverse action The whole chlorine would, therefore, soon have passed through the form HCl. Hence, by another mechanical arrangement, an action which ordinarily could progress to only 20 per cent would be turned into a complete one:

* The hydrogen chloride would be destroyed by interaction with the marble:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O.$$
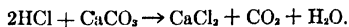
The calcium chloride is a solid. The gas, carbon dioxide, does not interact with the other substances, and would not, therefore, interfere with the for-mation of fresh hydrogen chloride.

$$2Cl_2 + 2H_2O \rightleftarrows O_2 + 4HCl(+ CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2).$$
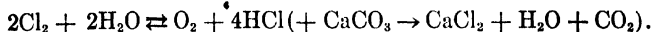
Reversibility Usually Avoided. — In every-day chemical work, since our object is usually to prepare some one substance, chemists either avoid chemical changes which are notably reversible, or adjust the conditions, as is done in the foregoing illustrations, so that the reverse of the action which they desire is prevented. In consequence of this, when carrying out the directions for making familiar preparations, the fact that such actions are reversible at all very readily escapes our notice. Arranging the conditions so that the separation of a solid body by precipitation, or the liberation of a gas, takes place, are the two commonest ways of rendering a reversible action complete. Excellent examples of both of these are furnished by the chemical change used in producing hydrogen chloride by the interaction of salt and sulphuric acid, the full discussion of which (p. 163) should now be studied attentively in the light of these explanations.

History. — The conceptions discussed in this chapter are not new, although they have come into general use rather recently. The law of reaction speed, and the influence of the concentrations of the reacting substance thereon (p. 210), was set forth and formulated by Wilhelmy as early as 1850. Gladstone (1855) studied quantitatively the influence of concentration in cases of chemical equilibrium (p. 209). The kinetic explanation (p. 206) was developed by Williamson (1851). Finally, the laws of chemical equilibrium were formulated more explicitly and applied more thoroughly by two Norwegian chemists, Guldberg and Waage (1864-9).

The Influence of Temperature on the Speed of any Reaction. — The activity of chemical change, and therefore the speed of all chemical changes, is increased by raising the temperature and diminished by lowering it (see p. 68). Thus, zinc displaces hydrogen more rapidly from hot than from cold hydrochloric acid. Iron rusts very much faster when heated than when cold. Different actions are affected in different degrees, and no simple rule accurately defining the effect can be given. Roughly speaking, however, a rise of 10° doubles the speed of every action. A

rise of 100° will therefore make the speed roughly **1024 times** greater. Hence, when the chemist finds that two substances show no evidence of interaction, he infers that there must be either slow action or none, and he seeks to settle the question quickly by heating the mixture.

The Influence of Temperature on a System in Equilibrium. — In a reversible change the two opposing reactions *are different actions* and their speeds are therefore affected *in different degrees* by the *same* alteration in temperature. Hence, when the temperature is changed, the relative amount of the two sets of materials present is altered and the equilibrium is displaced. Thus, in Deacon's process, a rise of 40° in the temperature displaces the equilibrium backwards (p. 208), and diminishes the yield of chlorine by 5 per cent. In the vapor of phosphorus pentachloride (p. 122), the displacement is in the opposite direction. At 200° and 760 mm. pressure, 51.5 per cent of the material is present as pentachloride and 48.5 per cent as trichloride and chlorine. Raising the temperature to 250° changes the proportions to 20 per cent and 80 per cent, respectively. At 330° only 3 per cent of the pentachloride remains. Evidently, here, raising the temperature favors the decomposition of the pentachloride, and therefore increases the speed of its dissociation more than it does the speed of the reunion of the trichloride and chlorine.

Van't Hoff's Law. — Now the facts mentioned above are connected by a law which will answer many practical questions in chemistry.

When phosphorus trichloride and chlorine combine to form PCl_5, *heat is given out.* Conversely, when phosphorus pentachloride dissociates, *heat is absorbed:*

$$PCl_5 + 30,000 \text{ calories} \rightleftarrows PCl_3 + Cl_2.$$
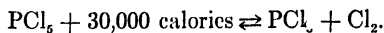
Now, when the temperature is *raised*, the action proceeds in the direction of decomposing more of the pentachloride. That is, the equilibrium is displaced in the direction which *absorbs heat.*

In Deacon's process, we find that the interaction of hydrogen chloride and oxygen *liberates heat,*

$$4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2 + 28{,}000 \text{ calories.}$$
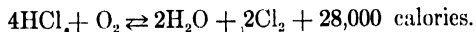
and in this action *raising* the temperature drives the equilibrium backwards, and a *lowering* in the temperature is required to increase the yield of chlorine.

The rule is obvious, and applies to all reversible reactions: When the temperature of a system in equilibrium is raised, the equilibrium point is displaced in the direction which absorbs heat. In other words, a rise in temperature favors the interaction of that one of the two sets of materials to which the heat is *added* (+ sign) in the equation. If the equation happens to be written with a negative heat of reaction (*e.g.*, p. 202), the heat can, of course, be transferred to the other side with its sign changed. This law is known as **Van't Hoff's law of mobile equilibrium.**

This law is of practical value. More than once, in chemical factories, much time and money have been spent on trying to arrange machinery to give a better yield of some substance at a high temperature, when a reference to this law would have shown that the chief change necessary was to use a lower temperature. We shall frequently have occasion to refer to this law in connection with industrial processes.

Application to Physical Equilibria. — Van't Hoff's law applies also to physical equilibria. Thus, the vaporization of a liquid absorbs heat, and so an increase in temperature will increase the pressure, and therefore the concentration of its vapor. The special case of a *saturated solution* may be somewhat more fully considered.

When we heat a saturated solution, with excess of solid present, more solid will dissolve as the temperature is raised, if solution is attended with absorption of heat. This is the usual case, as is shown by the way in which most solubilities increase with rising temperature. The solution of a solid in a liquid, indeed, may be regarded in ideal cases (see p. 144) as equivalent to the process of fusion, which, like vaporization, always absorbs heat. The precipitation of crystals from a supersaturated

solution, similarly, may be considered as analogous to the solidi-
fication of a pure substance, the freezing-point being depressed
below the normal value, however, by the presence of the solvent
(see p. 155). *Freezing-point lowering and solubility phenomena
are therefore identical.* When we determine the depression of the
freezing-point of water on addition of sugar·by noting at what
temperature ice begins to separate out, we measure, simultane-
ously, the *solubility of ice* in the solution at that temperature.
In the same way, when we determine the solubility of sugar in
water at 25°, we establish also how much water must be added to
a given quantity of sugar to depress the freezing-point of sugar
to 25°. It is therefore just as correct to say that sugar melts in
tea as it is to say that ice melts in iced tea.

Often, however, extensive chemical reactions occur in the pro-
cess of solution (see p. 145), and the heat effect of these reactions
may be considerable. Thus when water is added to concentrated
sulphuric acid, so much heat is evolved that the water boils.
In the case of a few salts, also, we find that solution in water
takes place with evolution of heat, and we draw the conclusion
that the heat of the chemical reactions involved *more than coun-
terbalances* the heat absorbed in the process of fusion.

When we heat a saturated solution, with excess of solid pres-
ent, crystals will separate out as the temperature is raised, if
precipitation is attended by absorption of heat. This is the case
with anhydrous sodium sulphate Na_2SO_4 and some calcium salts
in water (see p. 147).

Le Chatelier's Law. — The above-mentioned law is really a
particular case of a more general one, the law of Le Chatelier.
If some stress (*e.g.*, by change of temperature, pressure, or con-
centration) **is brought to bear on a system in equilibrium, a reac-
tion occurs, displacing the equilibrium in the direction which tends
to undo the effect of the stress.** Thus, raising the temperature
furthers the change which absorbs heat — and therefore would
tend to lower the temperature. Increasing the concentration
of the molecules pushes the action in the direction which uses up
these very molecules (p. 209). Again, pressure causes ice to melt,
because the water which is formed occupies a smaller volume, and

this change tends to relieve the pressure. But pressure will not cause most substances to melt, because usually the liquid form occupies a greater volume and its production would tend to increase pressure.

The student is cautioned against applying these laws to systems *not in equilibrium*, for example, to *unsaturated* or *supersaturated* solutions. To such cases they do not, necessarily, apply. Thus the addition of a small quantity of cupric chloride to water is attended by evolution of heat. It would be quite wrong to reason from this, however, that the solubility must fall off as the temperature is raised. The salt is extremely soluble in water, and if we keep on adding it to the solution until the latter is saturated we find that the last portions dissolve with absorption of heat. Now it is *only the saturated solution that is in equilibrium with the solid*, hence it is only with respect to this solution that we can apply Van't Hoff or Le Chatelier's law. In accordance with the behavior of this solution, we find that the solubility *increases* with rising temperature.

The characteristics of systems in equilibrium (pp. 78, 207) should therefore be kept in mind carefully, in order to avoid mistakes.

Summary. — In this chapter we have answered three questions:

1. Why do some chemical actions cease, while still far from complete? Answer: They are reversible.

2. What explains the position of the equilibrium point? Answers: (a) Equal effects of opposed molecular actions; (b) Equality in speed of opposed reactions.

3. What will displace the equilibrium point? Answer: (a) Change in concentration of one (or more) of the substances; (b) Change in the temperature; (c) Change in the pressure.

Exercises. — 1. Explain the apparent completeness of the action by which hydrogen chloride and water, respectively, are formed by direct union of the elements.

2. Explain the apparent completeness of the action by which silver chloride (p. 167) is formed.

3. Explain why the decomposition of potassium chlorate is complete.

4. In view of the statements on 'p. 19, explain why mercuric oxide is completely decomposed by heating.

5. Why can magnetic oxide of iron be reduced completely by a stream of hydrogen (p. 68), and iron oxidized completely by a current of steam (p. 60)?

6. With the phosphorus pentachloride system, say at 250°, what effect would suddenly enlarging the space containing a given amount of the vapor produce? What would be the effect of diminishing the space? What would be the effect of introducing additional chlorine into the same space (p. 209)?

7. Are the following systems in equilibrium or not: (a) a captive balloon pulling at its rope, (b) a balloon floating freely in cooling air, (c) a man wearing a heavy suit in winter only, (d) a woman changing to a velvet hat in August and to a straw hat in February? What is the stress in each case? In which systems does a reaction take place which opposes the effect of the stress?

8. What inference should you draw from the fact that (a) the solubilities of potassium nitrate and of sodium sulphate decahydrate in water increase with rise in temperature; (b) those of calcium hydroxide (p. 147) and ether decrease with rise in temperature?

9. By what practical means could the degree of dissociation of phosphorus vapor from P_4 to P_2 at 1700° (p. 122) be diminished, without changing the temperature?

CHAPTER XVI

ACIDS, BASES AND SALTS

THE employment of interacting substances in the form of solutions is so constant in chemistry, and the reasons for this are so cogent, that we must now resume the discussion of this subject.

Acids, Bases and Salts. — In a preceding chapter (Chapter XII) we have examined the properties of two interesting derivatives of common salt NaCl, namely hydrogen chloride HCl and sodium hydroxide NaOH. The former of these, when dissolved in water, was found to exhibit a set of properties (p. 167) which were stated to be characteristic of all substances called **acids.** Its aqueous solution is therefore given a distinctive name, **hydrochloric acid.** The second substance, sodium hydroxide, when dissolved in water, was similarly shown (p. 171) to possess a number of properties which were stated to be characteristic of all substances called **alkalies or bases.**

When hydrochloric acid and sodium hydroxide interact, sodium chloride NaCl is regenerated:

$$HCl + NaOH \rightarrow NaCl + H_2O.$$
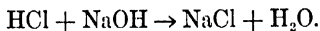
This action is not peculiar to hydrochloric acid and sodium hydroxide (see p. 167). **Acids in general** react with **bases in general** to give substances which, in aqueous solution, possess certain properties quite different from those of either acids or bases. They show, instead, striking resemblances to common salt. On account of these resemblances, they are called **salts.**

Before examining in greater detail the properties of acids, bases and salts in solution, let us first recall the names and formulæ of some of the examples of these classes that we have already had occasion to mention.

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Some Familiar Acids. — The following are some of the acids we have mentioned:

Hydrochloric acid	........HCl	Nitric acid	...........HNO₃
Sulphuric acid	..........H₂SO₄	Hypochlorous acid	....HOCl
Phosphoric acid	.........H₃PO₄	Acetic acid	.........HCO₂CH₃

Hydrochloric acid ....HCl   Nitric acid ....HNO_3
Sulphuric acid ....H_2SO_4 Hypochlorous acid ....HOCl
Phosphoric acid ....H_3PO_4 Acetic acid ....HCO_2CH_3

Familiar Bases. — The bases mentioned, with one or two additions (in *italics*), are:

Sodium hydroxide ....NaOH   Calcium hydroxide ......$Ca(OH)_2$
Potassium hydroxide ......KOH   Cupric hydroxide ....$Cu(OH)_2$
Ammonium hydroxide ....NH_4OH *Zinc hydroxide* ....$Zn(OH)_2$

Familiar Salts. — Some of those already mentioned are:

Sodium chloride ....NaCl   Potassium chlorate ....$KClO_3$
Sodium sulphate ....Na_2SO_4 Zinc sulphide ....ZnS
Potassium nitrate ....KNO_3 Sodium peroxide ....Na_2O_2
Ammonium chloride ......NH_4Cl Sodium carbonate ....Na_2CO_3
Cupric sulphate ....$CuSO_4$ Lead sulphide ....PbS

Radicals. — Upon comparing the formulæ in the above lists, we notice that:

1. Every acid contains hydrogen, combined with one or more other atoms, which constitute a group called a **radical.**

2. The very same radicals that are combined in acids with hydrogen, such as SO_4, appear also in *salts.*

3. Every base contains OH (the radical **hydroxyl**), and usually one atom, but occasionally more than one (as in NH_4) in the other radical.

4. The same radicals that are combined in bases with OH appear also in salts.

5. Radicals may be simple, like H, Na, and Cl, or compound, like SO_4 and NH_4.

6. In all cases, the quantities of the two radicals present must possess **identical total valence** (see p. 130). Thus one bivalent radical, such as Zn, combines with *two* univalent radicals, such as Cl or NO_3, but with *only one* bivalent radical, such as SO_4.

Positive and Negative Radicals. — When the electric current is passed through an aqueous solution of an acid, such as hydrochloric acid (p. 65), the acid is decomposed and hydrogen is

liberated at the *negative* electrode. Since this electrode attracts *positively charged particles*, hydrogen is called a *positive radical* (p. 61). (In all circumstances, unlike charges of electricity attract, and like charges repel one another.) The rest of the acid molecule, such as Cl, is attracted to the *positive* electrode, and is therefore called a *negative radical*. Similarly, when we electrolyze a solution of a base, such as sodium hydroxide, oxygen is always liberated at the *positive* electrode. This is due to the decomposition of the hydroxyl radical OH, which is consequently also a *negative* radical:

$$4OH \rightarrow O_2 + 2H_2O.$$
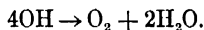
The rest of the alkali molecule, such as Na, is attracted to the *negative* electrode and is therefore a *positive* radical.

In the same way every salt contains a positive radical, other than H, combined with a negative radical, other than OH. The name of each salt indicates the radicals of which it is composed.

As regards the salts in the second column, they show positive radicals, like K, Zn, and Na, found in the list of bases. The negative radicals ClO_3, S, O_2, and CO_3 are not in the list of acids we have met with. But there are well-known acids corresponding to them, namely, chloric acid $HClO_3$, hydrogen sulphide H_2S, hydrogen peroxide H_2O_2, and carbonic acid H_2CO_3.

In general, then, all positive radicals combine with OH to give bases, all negative radicals combine with H to give acids. In general, also, each positive radical will combine with any negative radical to give a salt. In a few exceptional cases only, the compound cannot be formed, presumably because it is unstable under ordinary conditions.

Properties Common to Acids, Bases and Salts in Solution. — There are *four* of these properties, all of which have come up previously.

1. **Displacement.** — A *simple* radical belonging to an acid, base, or salt in solution can be *displaced* by another element, and is thereby obtained in the free state. Thus we have already seen (p. 62) that hydrogen is liberated from acids by the addition of the more active metals:

$$Zn + 2HCl \rightarrow H_2 + ZnCl_2.$$
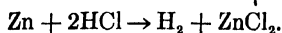
Exactly the same type of reaction takes place when we add to the solution of a *salt* any metal higher up in the activity series than the positive radical of the salt. For example, zinc will displace copper from a solution of cupric sulphate *or any other soluble cupric salt:*

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu.$$
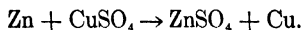
The copper is obtained as a red precipitate. This principle is extensively used in the purification of the more valuable metals at the foot of the activity series (p. 64). Thus copper will displace silver, and silver will displace gold, from solutions of their respective salts.

Similarly, a simple *negative* radical can be displaced by a more active element. Thus the iodide radical in potassium iodide is displaced by gaseous chlorine, iodine being liberated (see p. 181):

$$2KI + Cl_2 \rightarrow 2KCl + I_2.$$
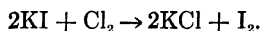
2. Double Decomposition. — Several examples of this type of reaction between acids, bases and salts in solution have already been discussed (pp. 162, 167, 171 and 209). In fact, whenever two solutions of such substances, which contain no radical in common, are mixed, a double decomposition occurs. Any acid or base will therefore react with any salt of a different acid or base. Any acid will give a reaction with any base. Salts containing no common radical will also react in pairs.

Very frequently we obtain instant evidence of such reactions by the appearance of a *precipitate,* one of the products formed being only slightly soluble in water. For example:

. Salt and acid:	$AgNO_3 + HCl \rightarrow AgCl \downarrow + HNO_3$	(1)
Salt and base:	$CuCl_2 + 2NaOH \rightarrow Cu(OH)_2 \downarrow + 2NaCl$	(2)
Acid and base:	$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 \downarrow + 2H_2O$	(3)
Salt and salt:	$AgNO_3 + NaCl \rightarrow AgCl \downarrow + NaNO_3$	(4)
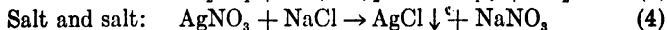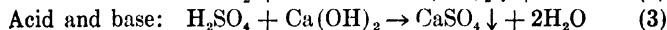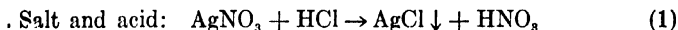
Such precipitations furnish us with very useful **tests** for establishing the presence or absence of certain radicals in an unknown substance. For example, a curdy white precipitate of silver

chloride is obtained not only by adding to a solution of silver nitrate a solution of hydrochloric acid (equation 1) or sodium chloride (equation 4), but by addition of *any solution containing the radical Ag to any solution containing the radical Cl*. If we suspect that a solution contains Ag, we add, therefore, a solution of any chloride. If we suspect that a solution contains Cl, we add a solution of any soluble silver salt. In either case a negative result is conclusive evidence of the absence of the radical tested for. If a positive result is obtained, the precipitate must be examined further, to prove whether or not it is silver chloride.

Even when no precipitate appears, however, *some* interaction takes place. Thus a solution obtained by mixing sodium nitrate and potassium chloride solutions is identical in all its properties with a solution obtained by mixing sodium chloride and potassium nitrate solutions. The appearance of a precipitate is *not*, therefore, an essential feature of a double decomposition. The most important point for us to notice is that, in all such reactions, each substance present behaves exactly as if it consisted of *two distinct radicals*. We may therefore regard double decompositions as a simple result of *the liberty of radicals to interchange partners*. Normally, this exchange will not be complete. Thus in the instance cited immediately above we have the reversible reaction:

$$(Na)(NO_3) + (K)(Cl) \rightleftarrows (Na)(Cl) + (K)(NO_3).$$
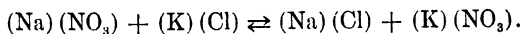
Whichever pair of salts we start with, we reach the same result on mixing their solutions. Every double decomposition is similarly reversible in theory, and gives an *equilibrium mixture*. But because, in many mixtures, one of the four possible compounds *withdraws from the exchange of partners* by disappearing from the solution either as a gas (p. 162) or as a precipitate (p. 163), the reaction in such cases becomes practically complete in one direction.

Another significant point may now be noted. Not only does every acid, base and salt in solution behave, in double decompositions, as if it consisted of *two distinct radicals*, but it can be shown to possess *two independent sets of properties*, one referring to each radical. Thus a solution of cupric chloride in water

exhibits one set of properties which can be referred directly to the cupric radical, and which is accordingly not peculiar to cupric chloride, but is common to all cupric salts in aqueous solution. To mention only two of these: (1) the color of the solution, when diluted with water, is *blue,* and (2) the addition of a base gives a pale blue, gelatinous precipitate of *cupric hydroxide* (see equation 3 above). The same solution exhibits a second set of properties which can be referred directly to the chloride radical and which is consequently common to all chlorides. To mention only two of these again: (1) when the solution is heated with concentrated sulphuric acid, HCl is evolved (see p. 162), and (2) the addition of a silver salt gives a precipitate of *silver chloride.*

The properties of acids (p. 167) are properties of the *hydrogen radical.* The properties of bases (p. 171) are properties of the *hydroxyl radical* OH.

A *radical,* then, is *an atom, or group of atoms, which behaves as a distinct unit in double decompositions, and which confers a definite independent set of properties upon solutions of all acids, bases or salts of which it forms one constituent.* Simple radicals also behave as separate units in *displacements.*

3. Conductivity. — Solutions of acids, bases, and salts in water are *all* conductors of electricity. Acids, bases and salts are therefore called "electrolytes." *In all cases* the solution is decomposed by the passage of the current. The positive and negative radicals of which the solute is composed are attracted to the opposite electrodes. There, unless special circumstances prohibit (see, for example, the electrolysis of sodium chloride, p. 169), they are liberated. Thus, all acids give hydrogen at the negative pole, the other radical passing to the positive pole.

Of all the properties they have in common, this one of being electrolytes is perhaps the most remarkable. It appears more surprising when we consider that *no* substances, other than acids, bases, and salts, undergo electrolysis in aqueous solution. This is an exclusive property of these classes of bodies.

The conducting power of solutions can be examined, roughly, by the apparatus in Fig. 71. The platinum electrodes are connected with a direct-current circuit. The lamp, which is on one

of the wires, serves, by its resistance, to cut down the current.
Its glowing also shows when the liquid is a conductor, and by
varying brightness indicates roughly the conducting power of the
solution.

A solution of sugar in water shows no conductance, and the
lamp remains dark. Solutions of acids, bases, and salts in water
enable the lamp to glow.
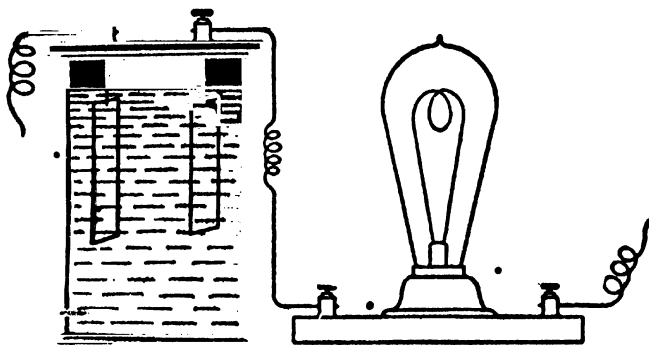
FIG. 71.

We quickly find that different solutions, when they conduct,
do so in different degrees. Solutions of hydrochloric and nitric
acids conduct well. So do solutions of sodium and potassium
hydroxides. Salt solutions are practically *all* good conductors.
But many acids, like acetic acid, conduct poorly in aqueous solu-
tion. The same is true of some bases, like ammonium hydroxide.

Of course, acids, bases, and salts which are only very slightly
soluble in water give poorly conducting solutions. But in esti-
mating the conductivity for chemical purposes, we have to take
into consideration the amount dissolved. Thus silver chloride,
being a salt, is an excellent conductor, when we allow for the
extreme diluteness of the solution. A *saturated solution* of silver
chloride, in point of fact, shows a slightly higher conductance
than a solution of sodium chloride of the same concentration.

Substances which give solutions with high conducting power

are called **strong electrolytes.** Substances which give poorly con-
ducting solutions are called **weak electrolytes.**

4. Vapor Pressures; Boiling-Points; Freezing-Points. — We
have seen (pp. 153-155) that equal numbers of molecules of differ-
ent solutes dissolved in equal weights of water normally depress
the vapor pressure, raise the boiling-point, and lower the freezing-
point by constant amounts. Thus, one molecular weight of sugar
(342 g.) or of glycerine (92 g.) dissolved in 1000 g. of water will
raise the boiling-point from 100° to 100.52°, and will lower the
freezing-point from 0° to – 1.86°. But this is uniformly true
only of *non-conducting solutions,* in other words, solutions of
substances which are not acids, bases, or salts. Gram-molecular
weights of substances of these three classes, dissolved in 1000 g.
of water, raise the boiling-point more than 0.52 degrees and lower
the freezing-point by more than 1.86 degrees. We say they give
abnormal elevations of the boiling-point and *abnormal* lowerings
of the freezing-point. Vapor pressure depressions in such solu-
tions are also *abnormal.*

Thus, a solution of 58.46 g. of sodium chloride in 1000 g. of
water boils at 100.97°, and freezes at – 3.42°. The elevation in
the boiling-point of the water is 0.97° instead of 0.52°. The de-
pression of the freezing-point is 3.42° instead of 1.86°. The
effect in each case is *nearly twice* as great as the normal one.
In the same way, a gram-molecular weight of potassium chloride
dissolved in 1000 g. of water at 20° depresses the vapor pressure
by 0.554 millimeters, while a gram-molecular weight of mannite
(a normal sugar which gives a non-conducting solution) in the
same amount of water lowers the vapor pressure by only 0.313
mm. Again the effect is nearly twice the normal.

The only conclusion we can draw from these results is that
nearly twice the normal numbers of solute molecules are present
in such solutions. In other words, not only do we have two in-
dependent sets of properties exhibited by the constituent radicals
in solutions of electrolytes, but these same solutions actually
behave as if the radicals were, to a large extent, uncombined with
each other. It appears as if sodium chloride, for example, is

largely *decomposed* in aqueous solution into independent sodium and chloride radicals. Additional evidence in this direction is supplied by the behavior of electrolytes of more complex types, such as sodium sulphate Na_2SO_4 or zinc chloride $ZnCl_2$. Both of these substances, in dilute solution, give boiling-point and freezing-point changes which are nearly *three times* the normal, indicating that they are largely decomposed into their three constituent radicals ($2Na$ and SO_4; Zn and $2Cl$). In the same way, substances containing four radicals, like ferric chloride $FeCl_3$, give effects approaching *four times* the normal in dilute solution.

One last point remains to be mentioned. It has been noted above that some acids, like acetic acid, and some bases, like ammonium hydroxide, are only poor conductors in solution. Just these same two classes of substances, it has been found, give only very slightly abnormal changes in the three physical properties of solutions here under examination. The full significance of this difference in behavior will appear in the following chapter.

A Warning. — The reader is urged to keep in mind the fact that it is *only in solution* (and particularly in *aqueous solution*) that the special properties of acids, bases, and salts become apparent. Their behavior is often quite different in the absence of a solvent. If, for example, we mix together dry ammonium carbonate $(NH_4)_2CO_3$ and partially dehydrated, solid cupric nitrate $Cu(NO_3)_2$, and apply heat, a violent interaction begins. This interaction is nothing so simple as a double decomposition, however. An immense cloud of smoke and gas is thrown out of the tube, and the solid remaining is either black or reddish, in parts, according to the proportions of the substances employed. This residue contains black cupric oxide CuO, and sometimes red cuprous oxide Cu_2O. The gas evolved is tinged red by the presence of nitrogen peroxide NO_2, while a careful analysis would show that it contained also carbon dioxide CO_2, nitrogen N_2, nitrous oxide N_2O, water vapor H_2O, and perhaps still other products.

The contrast, when the substances are dissolved in water before being brought in contact, is very great. A pale green precipi-

tate is immediately produced, which rapidly settles out and proves, on examination, to be a carbonate of copper. Evaporation of the solution gives us ammonium nitrate.

$$(NH_4)_2CO_3 + Cu(NO_3)_2 \rightarrow CuCO_3 \downarrow + 2NH_4NO_3.$$
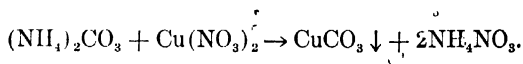
The reaction is essentially a double decomposition (although, strictly speaking, the precipitate is not the normal carbonate of copper, but a *basic* salt, see p. 247), similar in character to those already discussed.

The differences in properties between *dry hydrogen chloride* and *hydrochloric acid* (p. 166) furnish another good example of the fundamental changes involved in the addition of water as a solvent. Carefully dried hydrogen chloride has practically none of the properties of an acid. It does not affect litmus, it does not conduct the electric current. It is true that it does react with the more active metals (such as Na or K), hydrogen being displaced and the chloride of the metal formed. But it is probable that even this property would disappear if we could succeed in eliminating the last traces of moisture from our reacting products. A solution of *sulphuric acid* acts on sodium so vigorously that the mixture explodes, but pure hydrogen sulphate H_2SO_4, when very carefully dehydrated, is so inert that metallic sodium floats in it without the slightest evidence of any interaction.

The rules that have been derived in the preceding sections regarding the behavior of acids, bases, and salts in solution will be found to clear the ground wonderfully in the development of subsequent chapters, for the substances which we shall meet with, that are *not* included in the above groups, are very few indeed. Furthermore, since we naturally prefer, when we carry out a reaction either on a small scale in the laboratory or on a large scale in chemical industry, to have it under our control as much as possible, we contrive to perform most chemical changes with our reacting materials *in solution*. By this means we are enabled, in general, to forecast the course of the reaction accurately, to arrange the conditions so that the reaction will be sure to proceed smoothly, and to isolate without much difficulty those products which we desire to obtain in a pure state. In the absence of a

solvent a reaction is much more liable to get out of hand, perhaps explosively, with the result that the proper conditions of the process are not maintained, and we obtain either a poor yield or an impure product.

Non-Electrolytes. — The aqueous solutions of some substances (chiefly compounds of carbon, such as sugar) do not conduct the electric current any better than water, see p. 227). Such substances are called **non-electrolytes**. Even although a non-electrolyte may contain hydrogen, hydroxyl, or other characteristic groups in its usually rather complex molecule, its solution exhibits none of the properties of acids, bases or salts developed in the preceding pages. Thus alcohol C_2H_5OH is *not* a base; nitroglycerine $C_3H_5(NO_3)_3$ is *not* a salt. The vapor-pressure depressions, boiling-point elevations and freezing-point lowerings obtained with such non-conducting solutions are never abnormally great. If any deviation is observed, it is always in the other direction, an abnormally small change indicating that the substance is partially *associated* (see p. 145) in aqueous solution.

Non-electrolytes do not show any pronounced change in behavior when dissolved in water. Sugar, for example, is, as a rule, more readily acted upon in the absence of any solvent. Then again, while water is not the only solvent which has the effect we have just described, the majority of solvents, if they affect chemical change at all, simply retard it. Thus the union of iodine and phosphorus in the absence of a solvent takes place spontaneously with a violent evolution of heat. When the elements are dissolved in carbon bisulphide, before being mixed, the action is much milder, although the product is the same (phosphorus tri-iodide). The diminution in the concentration of the ingredients has decreased the speed of the action in the normal way (p. 210).

Exercises. — 1. By what experiments should you determine which were the radicals in substances of the following composition:

$Cu(NO_3)_2$, $CaCO_3$, NH_4Br, NH_4I, $KClO_4$ and $KMnO_4$.

There are always two ways, and usually three, of determining the radicals — what are they (pp. 223-224)?

2. How should you determine whether a given substance were an acid, a base, a salt, or a non-electrolyte?

3. Make equations showing the interactions of solutions of aluminum chloride $AlCl_3$ and of cupric sulphate $CuSO_4$ with sodium hydroxide (p. 171). Name the products.

4. Make equations showing the interactions of solutions of zinc chloride $ZnCl_2$ and of ferric chloride $FeCl_3$ with silver sulphate Ag_2SO_4. Name the products.

5. What is the action of metallic zinc on solutions of sodium chloride, lead nitrate $Pb(NO_3)_2$, silver sulphate Ag_2SO_4, magnesium sulphate $MgSO_4$, mercuric chloride $HgCl_2$?

CHAPTER XVII

WE have learned in the preceding chapter that acids, bases, and salts in solution exhibit two independent sets of properties, one of which can be referred to the *positive*, the other to the *negative radical*. We have seen that the passage of an electric current through such a solution decomposes it, the positive radical of the electrolyte proceeding to the negative electrode, the negative radical to the positive electrode. Finally, we have found that the abnormalities in certain physical properties of these solutions seem to indicate that the radicals actually exist, to a large extent, in an *uncombined* state in the solution.

Upon these facts a hypothesis has been based which has proved of considerable assistance in explaining the special properties of conducting solutions. The fundamental idea of this hypothesis, which was first definitely advanced by the Swedish chemist Arrhenius in 1887, is now accepted as an established fact. Our knowledge of the field of conducting solutions is still, however, very imperfect, and many important deductions from the hypothesis of Arrhenius remain matters of conjecture and dispute.

The Ionic Hypothesis. — In this hypothesis of Arrhenius it is assumed that the molecules of an electrolyte, such as hydrogen chloride, are largely broken up in solution into their constituent radicals, *each radical being electrically charged.* These charged radicals have been called *ions*, and the hypothesis is hence known as the ionic hypothesis. A solution of hydrogen chloride in water is supposed therefore to consist of two parts: (1) an undissociated part, made up of hydrogen chloride molecules HCl; (2) a dissociated or ionized part, made up of equal numbers of hydrogen atoms carrying a positive charge (H+) and

chlorine atoms carrying a negative charge (Cl⁻). That portion of the hydrogen chloride which remains undissociated in solution is understood to be *inactive.* It plays no part in the conduction of the current, it exerts a normal effect on the physical properties of the solution (vapor pressure, boiling-point and freezing-point changes), it does not convey to the solution any of the properties of an *acid,* it takes no direct share in displacements or double decompositions. That portion of the hydrogen chloride, on the other hand, which breaks up into hydrogen ions H⁺ and chlorine, ions Cl⁻ is *active.* All of the special properties of the solution may therefore be referred to these ions, as we shall see below.

Ionic Equations. — Of course, there is an equilibrium between the undissociated and dissociated parts of an electrolyte in solution, and this equilibrium may be represented by the ionic equation:

$$HCl \rightleftarrows H^+ + Cl^-.$$
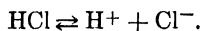
Ionization is, therefore, a kind of decomposition or rather dissociation, and is in every sense a chemical change. In ionic equations the *charges* upon the ions *must be shown,* as they are essential parts of the ionic substances.

Since the solution, as a whole, has itself no charge, **equal quantities of positive and negative electricity must be produced.** This means that bivalent radicals, on dissociation, will become ions carrying a double charge and trivalent ions must carry a triple charge:

$$CuCl_2 \rightleftarrows Cu^{++} + 2Cl^- \quad CuSO_4 \rightleftarrows Cu^{++} + SO_4^=$$
$$K_2SO_4 \rightleftarrows 2K^+ + SO_4^= \quad FeCl_3 \rightleftarrows Fe^{+++} + 3Cl^-$$
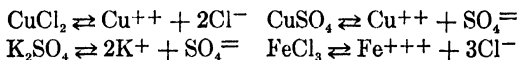
In these equations, the coefficients multiply the charges as well as the radicals bearing the charges, and it will be seen that the numbers of positive and negative charges produced by each dissociation are equal. Hence, **univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence.** This is an inevitable inference

Svante Arrhenius.

from the electrical neutrality of all solutions. An **ion** is therefore an **atom or group of atoms bearing an electric charge, or a number of such charges.**

• The positive ions are called the **cations,** since they move toward the negative electrode, or cathode. The negative ions are the **anions,** and move toward the positive electrode, or anode.

‚ **Ions and Electrolysis.** — Let us first attempt to understand the phenomena of electrolysis in the light of the ionic hypothesis. A solution of HCl in water contains three kinds of solute; un-
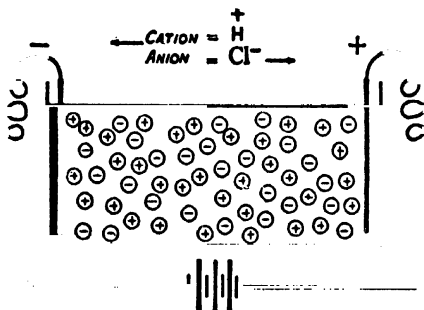
FIG. 72.

dissociated HCl molecules, positively charged hydrogen ions H^+, and negatively charged chlorine ions Cl^-. These are scattered indiscriminately throughout the solution, as indicated in Fig. 72 (only the two ions are there shown, the undissociated part is omitted since it plays no direct part in the electrolysis). Equilibrium is kept up by continual dissociation and recombination, according to the equation $HCl \rightleftarrows H^+ + Cl^-$.

As soon as the circuit is completed, all the ions in the solution begin to *migrate* towards their proper electrodes. The positively-charged hydrogen ions are attracted towards the negative electrode, the negatively-charged chlorine ions are attracted

towards the positive electrode. Two orderly processions of ions, moving in opposite directions, proceed therefore through the solution. Ions (Greek, *going*) derive their name from this fact.

The rest is easily understood. When a positive ion reaches and touches the negative electrode, its positive charge of electricity is neutralized, and the result is an ordinary atom of hydrogen. The atoms of free hydrogen unite to give molecules (H_2) and these form bubbles of the gas. Simultaneously the negative ions are discharged at the positive electrode, and the atoms of free chlorine unite to give molecules (Cl_2).

Meanwhile, in the body of the solution, the departure of the ions has disturbed the equilibrium $HCl \rightleftarrows H^+ + Cl^-$. The undissociated part HCl therefore continues to break up, attempting to re-establish equilibrium, until the electrolysis is complete.

By electrolysis of a solution of hydrochloric acid, therefore, we obtain hydrogen and chlorine. With some electrolytes the course of events is not so simple, secondary reactions taking place at the electrodes. Thus when we pass a current through a solution of sodium chloride, we obtain chlorine at the positive electrode, but hydrogen instead of sodium is liberated at the negative electrode (see p. 169). In the same way, when we electrolyze a solution of cupric sulphate, metallic copper is deposited on the negative electrode, but the radical SO_4 cannot exist in the free state, and reacts with the water present to liberate oxygen, according to the equation:

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2.$$
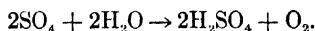
Even when we do not actually isolate the free radicals of an electrolyte by electrolysis, however, we can show that they have migrated with the current in the usual way by the fact that they collect around the electrodes. Thus, in the electrolysis of sodium chloride, the solution around the negative electrode becomes *alkaline,* owing to accumulation of sodium hydroxide. Similarly, in the electrolysis of copper sulphate, the solution around the positive electrode becomes *acid,* owing to accumulation of sulphuric acid.

Actual Quantities of Electricity Concerned. — In a previous paragraph (p. 234) we reached the conclusion that univalent ions all possess equal quantities of electricity, and other ions bear quantities greater than this in proportion to their valence. This conclusion is confirmed by actual measurement. When hydrochloric acid is electrolyzed, 35.46 g. ($=$ Cl) of chlorine are liberated for every 1.008 g. ($=$ H) of hydrogen. But when cupric chloride $CuCl_2$ is substituted, for every 35.46 g. ($=$ Cl) of chlorine set free, only 31.78 g. ($= \frac{1}{2}$ Cu $= \frac{1}{2}$ 63.57) of copper is deposited. The **law**, discovered by **Faraday**, is that **equal quantities of electricity liberate equivalent quantities of the 'ions** (equivalent, p. 64, *not* atomic or molecular).

The units of electrical energy are the **coulomb**, which is the unit of quantity, and the **volt**, which is the unit of intensity, or potential difference between the electrodes (*electromotive force*). Faraday's law has to do only with the former. Equal numbers of coulombs liberate equivalent weights of all elements, but different voltages are required to decompose different compounds, according to their stability (see Chap. XLVI).

To liberate 1.008 g. of hydrogen, or one equivalent of any other element, 96,540 coulombs of electricity are needed. The charges on 1.008 g. of hydrogen ions must, therefore, equal this amount. There are 6.06×10^{23} molecules of hydrogen in 22.4 liters (H_2) and therefore in 2.016 g. of the gas. A simple calculation shows therefore that each coulomb is distributed over about 63×10^{17} hydrogen ions.

A current of 1 coulomb per second is called **1 ampere.** Thus, the current passing through a 1-amp. lamp (or 2 half-ampere lamps in parallel) will liberate 1.008 g. (11.2 liters) of hydrogen in 96,540 seconds, or 26 hours and 49 minutes. The same current will liberate 107.88 g. of silver (Ag^I) from silver nitrate, or 31.78 g. of copper ($Cu^{II}/2$) from cupric sulphate in the same time. A current of 5 amperes will accomplish the same result in one-fifth of the time.

Ionic Migration. — A very convenient arrangement for observing the migration of ions is to dissolve copper sulphate in warm water containing about 5 per cent of agar-agar (a gelatine

obtained in China from certain sea-weeds), and to fill with this
mixture the lower part of a U-tube (Fig. 73). The setting of
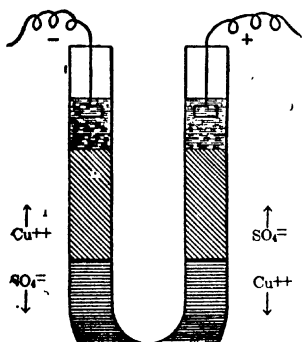
FIG. 73.

the jelly prevents subsequent
mixing with the rest of the fill-
ing of the tube, and the conse-
quent disappearance of the
boundary of the blue solution.
A few grains of charcoal are
scattered on the surface of the
jelly to mark the initial posi-
tion of this boundary in each
limb, and a warm solution of
some colorless electrolyte, such
as potassium nitrate, also con-
taining agar-agar, is added on
each side. When this has set, a
little potassium nitrate solution
in pure water is also added on

each side, and in this the electrodes are inserted. The whole is
finally placed in ice and water, to prevent melting of the jelly by
the heat caused by resistance, and the current is then turned on.

After a time, we observe that the blue cupric ions ascend
above the mark on the negative and descend away from it on
the positive side. In each case there is no shading off in the tint.
The motion of the whole aggregate of colored cations occurs in
such a way that, if the contents of the tube were not held in
place by the jelly, we should believe that a gradual transference
of the entire blue solution was being observed. With a current
of 110 volts, and a 16-candle-power (one-half ampere) lamp in
series with the cell, the effect becomes apparent in a few minutes.

Although the sulphate ions are invisible, we may safely infer
that they are drifting towards the positive electrode. Indeed,
this can be demonstrated by interposing a shallow layer of jelly
containing some barium salt a little distance above the charcoal
layer on the positive side. When the sulphate ions reach this,
barium sulphate $BaSO_4$ begins to be precipitated and the layer
becomes cloudy. In similar ways the progress of other colorless
ions may be rendered visible.

It appears, therefore, that electrolysis is not a local phenomenon, going on round the electrodes only, but that the **whole of the products of the dissociation of the solute are set in motion.**

Different ions move with different speeds. Under comparable conditions, the hydrogen ion is the most speedy, the hydroxyl ion comes next (see p. 242).* The speeds of all ions are individual properties and are independent of the nature of other ions that may be present, but are directly proportional to the rate of fall of potential between the positive and negative electrodes.*

By an experiment similar to the last, and devised by *А.* A. Noyes, the relative speeds of different ions may be demonstrated.
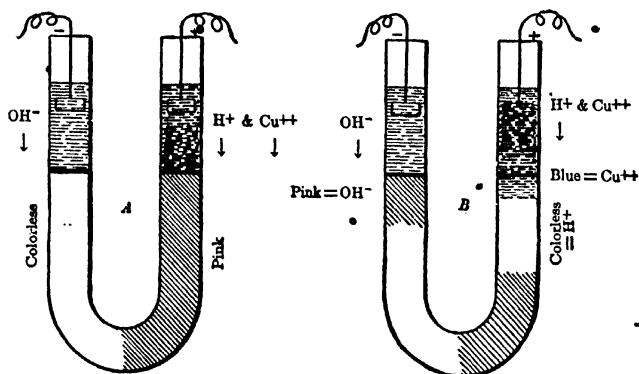
FIG. 74.

The U-tube (Fig. 74, showing the same tube *A* before the current starts, and *B* after it has been passing for some time) is partly filled with agar-agar jelly containing potassium chloride and phenolphthalein. On the right side, a drop of potassium hydroxide has been added to render the mixture pink. On the left, a drop of hydrochloric acid is present, and the mixture is colorless. Above the charcoal layer, in the right limb, a mixture of hydrochloric acid and cupric chloride, and in the left limb potassium hydroxide solution, are placed. The positive electrode is introduced on the right and the negative on the left. The hydrogen and copper ions drift away from the positive and

towards the negative electrode, the hydroxyl ions away from the negative and towards the positive electrode. The motion of the H^+ is marked by the disappearance of the pink color, that of the Cu^{++} by the advance of a blue layer, that of the OH^- by the progress of a pink coloration (see p. 172). By the time the hydrogen ions have been displaced $5\frac{1}{2}$ cm., the copper ions have moved 1 cm. and the hydroxyl ions about $2\frac{1}{2}$ cm. These distances indicate their relative *speeds of migration*.

Ions and Displacement. — When a metal acts upon a dilute acid, and hydrogen is liberated, it is the ions alone that are directly concerned in the mechanism of the action. Thus the equation for the action of zinc on hydrochloric acid may be written:

ELECTROMOTIVE SERIES OF THE METALS.
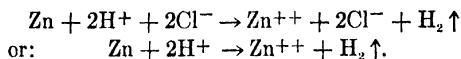
Potassium
Sodium
Barium
Calcium
Magnesium
Aluminium
Manganese
Zinc
Chromium
Iron
Cadmium
Cobalt
Nickel
Tin
Lead
Hydrogen
Antimony
Bismuth
Arsenic
Copper
Mercury
Silver
Platinum
Gold

$$Zn + 2H^+ + 2Cl^- \rightarrow Zn^{++} + 2Cl^- + H_2 \uparrow$$
or: $$Zn + 2H^+ \rightarrow Zn^{++} + H_2 \uparrow.$$

From this it appears (see, however, p. 267) that the action simply consists of a transfer of positive charges from hydrogen ions to atomic zinc, free hydrogen being liberated and zinc ion going into solution. Similarly the action of zinc on a solution of a copper salt may now be written:

$$Zn + Cu^{++} \rightarrow Zn^{++} + Cu \downarrow.$$
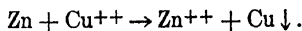
All the metals, indeed, can be set down in an order, such that each metal displaces those following it in the list and is displaced by those preceding it. This list is known as the **electromotive series** of the metals, because in electrolysis of solutions containing normal concentrations of these ions, the electromotive force of the current required to deposit each metal is less than that for the metal preceding in the list (see Chapter XLVI). For present purposes, the list shows the metals in **the order of diminishing tendency to enter the ionic from the elementary condition.**

The electromotive series embodies many facts in the behavior of the metals, and should be kept in mind as **furnishing a key to all actions involving solutions in which a free metal is used or produced.** It is, in fact, identical with the order of activity. (p. 64).

Ions and Double Decomposition. •— The mechanism of reactions of this type also becomes much clearer when we write the equations in the ionic form. Thus, for the precipitation of silver chloride by the action of hydrochloric acid on silver nitrate solution, we have: —

$$AgNO_3 \rightleftarrows Ag^+ + NO_3^-$$
$$HCl \rightleftarrows Cl^- + H^+$$
$$\uparrow\downarrow \qquad \uparrow\downarrow$$
$$AgCl \downarrow \quad HNO_3.$$
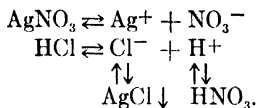
In the mixed solutions, we have **four** ions in quantity, Ag^+ and NO_3^- from the $AgNO_3$, H^+ and Cl^- from the HCl. Before mixing, these were in equilibrium with undissociated $AgNO_3$ and undissociated HCl respectively. But as soon as we bring all four ions into the same solution, we furnish them with the opportunity of combining with other partners, Ag^+ with Cl^- and H^+ with NO_3^-. Undissociated AgCl and undissociated HNO_3 are also present, therefore, in the mixed solutions, each substance in• equilibrium with its respective pair of ions. (This is conveniently indicated by the method of writing the equations which is employed above. The student should copy this method in analyzing all double decompositions.) The mixture contains, then, no fewer than **eight** different solutes, **four** ionic and **four** molecular, and **four** reversible reactions control the equilibrium relationships between them.

Now it so happens that one of the new solutes, AgCl, is *practically insoluble in water.* Unless the solutions are excessively dilute, therefore, silver chloride separates out from the solution as a *precipitate.* This precipitation disturbs the existing equilibria by withdrawing practically all silver ions Ag^+ and chloride ions Cl^- from the solution. Undissociated $AgNO_3$ and HCl continue to break up, in an attempt to re-establish the equilibria,

until they also are practically eliminated, and only hydrogen ions H^+ and nitrate ions NO_3^-, in equilibrium with undissociated HNO_3, are left in quantity in the solution.

The reader must note that *any* silver salt added to *any* chloride in solution also gives a precipitate of silver chloride. This can be *predicted* immediately by ionic equations. If, therefore, we learn the properties of a few important positive and negative ions, we learn, at the same time, the properties in solution of *all* the electrolytes of which these ions are constituents. This introduces a great simplification into the study of chemistry.

[1]To obtain the necessary practice in dealing with double decompositions, the student should now return to the section on these reactions in the preceding chapter (p., 224) and rewrite all of the equations there given or referred to *in full ionic form*. It is of great importance that the principles involved should be thoroughly understood in each case.

Ions and Conductivity. — Pure water is an exceedingly poor conductor of electricity. The high conducting power of a solution of an electrolyte is due, therefore, to the ions present. The actual conductance of any given solution will depend on the *number of ions* between the electrodes, the *number of charges upon each ion* (see p. 234), and the *rate at which the ions move.* The more numerous the ions are, and the more rapidly they migrate towards the oppositely-charged electrodes, the greater will be the number of discharges taking place per second upon each electrode.

The rate at which the ions move, under given conditions, has been carefully determined by methods which are refinements upon the experiments described on pages 238-240. It will suffice at this stage to give a few results. With electrodes one centimeter apart, and with a difference in electrical potential between the positive and negative electrodes of one volt, the velocities in centimeters per hour in dilute aqueous solution at $18°$ are as follows: H^+ 10.8, Na^+ 1.26, Ag^+ 1.66, OH^- 5.6, Cl^- 2.12, NO_3^- 1.91. The hydrogen ion is the fastest, the hydroxyl ion holds the second place.

With the help of these figures we can calculate what is the

extent of ionization of the electrolyte in any solution containing these ions, hydrogen chloride for example. We have already learned (p. 91) that a gram molecular weight of hydrogen chloride contains 6.06×10^{23} molecules. If ionization in solution were complete, therefore, a liter of a normal solution (p. 142) of hydrochloric acid would contain 6.06×10^{23} hydrogen ions, and the same number of chlorine ions. These, moving at the rates given above, would give a definite, calculable conductivity. The conductivity actually obtained by experiment with a normal solution of HCl at 18°, however, is only 78 per cent of this calculated value. The conclusion has been drawn that, in normal solution at 18°, hydrochloric acid contains only 78 per cent of free ions, the remaining 22 per cent of solute contributing nothing towards the conductivity. We may express this conclusion by writing the reversible ionic dissociation in the form:

$$(22\%) \; HCl \rightleftarrows H^+ + Cl^- \; (78\%)$$
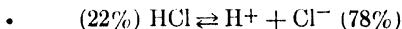
Equilibrium is reached in a normal solution of hydrochloric acid at 18°, therefore, when 78 per cent of the molecules are broken up into free ions.

At other concentrations different degrees of dissociation would be indicated. For example, a 10 N solution gives only 17 per cent of the calculated conductivity, a 0.1 N solution 92 per cent, a 0.01 N solution 97 per cent. *At very high dilutions, therefore, the ionization becomes practically complete.*

All electrolytes are not ionized to equal extents at the same concentrations. Thus, a normal solution of acetic acid at 18° shows only 0.4 per cent of the calculated conductivity for complete ionization. Even a 0.001 N solution is only 12.5 per cent ionized. A fundamental point in the ionic hypothesis of Arrhenius, however, is that ionization always approaches completion as the solution becomes more and more dilute.

The following table shows the approximate degrees of ionization of a number of typical electrolytes in tenth-normal solution in water at 18°. In the case of acids and bases containing more than one displaceable unit of hydrogen or hydroxyl, the kind of ionization on which the figure is based should be particularly noted.

FRACTION IONIZED IN 0.1 N SOLUTIONS AT 18°

ACIDS ,

Hydrochloric acid (H⁺,Cl⁻) ...0.92
Nitric acid (H⁺,NO₃⁻) 0.92ᵃ
Sulphuric acid (2H⁺,SO₄⁼) 0.6r
Oxalic acid (H⁺,HC₂O₄⁻) 0.50
Phosphoric acid (H⁺,H₂PO₄⁻) ..0.27

Hydrofluoric acid (H⁺,F⁻) ..0.085
Acetic acid (H⁺,CH₃CO₂⁻) ..0.013
Carbonic acid (H⁺,HCO₃⁻) ..0.0017
Hydrosulphuric acid (H⁺,HS⁻)0.0007
Boric acid (H⁺,H₂BO₃⁻) 0.0001

BASES

Sodium hydroxide
   (Na⁺,OH⁻) 0.91
Potassium hydroxide
   (K⁺,OH⁻) 0.91

Barium hydroxide (Ba⁺⁺,2OH⁻) 0.77
Ammonium hydroxide
   (NH₄⁺,OH⁻) 0.013

SALTS

Potassium chloride (K⁺,Cl⁻)...0.86
Sodium chloride (Na⁺,Cl⁻) 0.84
Potassium fluoride (K⁺,F⁻) 0.85
Sodium nitrate (Na⁺,NO₃⁻)....0.83
Potassium nitrate (K⁺ NO₃⁻)..0.83
Silver nitrate (Ag⁺,NO₃⁻) 0.81
Sodium acetate (Na⁺, CH₃CO₂⁻)0.79

Sodium bicarbonate
   (Na⁺,HCO₃⁻) 0.78
Barium chloride (Ba⁺⁺,2Cl⁻) ..0.76
Silver sulphate (2Ag⁺,SO₄⁼) ..0.70
Zinc sulphate (Zn⁺⁺,SO₄⁼) 0.40
Copper sulphate (Cu⁺⁺,SO₄⁼)..0.40
Mercuric chloride (Hg⁺⁺,2Cl⁻)<0.01

Ionization and Chemical Activity. — From a consideration of the above figures and the results given by other acids, bases and salts, the following important conclusions may be drawn:

1. Salts, with the exception of a few mercuric salts, are all *extensively ionized* in 0.1 N aqueous solution. The salts which dissociate into univalent ions show the greatest degree of ionization. Compare, for example, the series sodium chloride, silver sulphate, copper sulphate.

2. Acids show the most extreme differences in their degrees of ionization. That is to say, equivalent solutions contain very different concentrations of hydrogen ion. Since their *activity* as acids depends upon this substance (p. 246), it follows that acids will exhibit very marked differences in chemical activity (for example, in their action on metals). In fact, they may be divided roughly into three classes:

(a) *Strong acids,* such as hydrochloric acid, nitric acid, sulphuric acid. These substances are highly ionized in 0.1 N solution. Their solutions conduct the electric current excellently, and are chemically most active.

(b) *Transition acids,* such as phosphoric acid, hydrofluoric

acid. These substances are slightly ionized in 0.1 N solution. Their solutions conduct fairly well, and show moderate activity.

(c) *Weak acids*, such as acetic acid, carbonic acid, boric acid. These substances are scarcely ionized at all in 0.1 N solution. Their solutions conduct the current very poorly, and exhibit little activity as acids.

3. **Bases** also show very extreme differences in their degrees of ionization. We have two main classes — *strong bases*, such as sodium hydroxide, barium hydroxide; and *weak bases,* such as ammonium hydroxide. Between these fall certain *transition bases*, such as silver hydroxide (which is only very slightly soluble, but which is noticeably stronger than ammonium hydroxide) and some organic derivatives of ammonium hydroxide.

4. **Water** itself is both an exceedingly weak acid and an exceedingly weak base. It breaks up into the two ions H^+ and OH^- to a very minute extent indeed. At the ordinary temperature the fraction ionized is less than 0.000,000,002. Pure water consequently conducts the electric current practically not at all. The ionization of water, however, is a factor of vital importance in the explanation of certain reactions, as we shall see later.

Ions and Vapor-Pressure, Boiling-Point and Freezing-Point Abnormalities. — The cause of the abnormal changes in these three physical properties, exhibited by solutions of electrolytes, will now be evident. A solution of sodium chloride containing one-gram molecular weight of salt in 1000 g. of water gives almost *twice the calculated effect* in each case, because almost all of the solution is present as Na^+ and Cl^-, instead of as undissociated NaCl. The number of solute molecules present is almost *doubled* by ionization. Similarly a dilute solution of ferric chloride shows nearly *four times* the normal change in freezing-point lowering, for example, owing to the fact that the majority of $FeCl_3$ molecules are broken up into *four* ions, Fe^{+++} and $3Cl^-$.

Solutions of weak electrolytes, such as acetic acid and ammonium hydroxide, exhibit practically normal results, because only an insignificant fraction of the solute is broken up into ions.

Careful measurements show a close agreement in respect to

extents of ionization, as determined by the two independent methods, conductivity ratio and freezing-point depression, throughout the whole list of hundreds of electrolytes. Minor divergences exist in some cases which have not yet been entirely accounted for, but the agreement in general is so remarkably close that it cannot be a chance coincidence. We have here, in fact, very strong confirmation of the truth of the ionic hypothesis.

.The Properties of Acids. — The properties of *acids* (p. 167) are now seen to be properties of hydrogen ion H^+. An *acid* is a substance which contains hydrogen as a positive radical and, in solution, gives hydrogen ion. Strictly speaking, only the conducting solutions of such substances are acids, but for convenience we extend the term sometimes to include the pure substances. For example, HNO_3 is usually called nitric acid, not hydrogen nitrate.

Many substances, such as sugar $C_{12}H_{22}O_{11}$, contain hydrogen, but their solutions lack all of the properties of hydrogen ion. They therefore do not contain hydrogen as a radical, and are not acids.

A *strong acid* is one which is highly ionized in solution, and therefore shows the properties of hydrogen ion very markedly. A *weak acid* is one which is very little ionized in solution, and consequently exhibits the properties of hydrogen ion only feebly. Solutions of very weak acids (such as boric acid) scarcely affect blue litmus. Water, a still weaker acid, contains just as much hydroxyl ion OH^- as hydrogen ion H^+, and does not change the color of either blue or reddened litmus. Its acid properties are still evident, however, in its action on the most active metals, such as sodium:

$$Na + 2H^+ \rightarrow 2Na^+ + H_2 \uparrow.$$
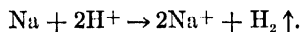
Acids are often classified according to the number of displaceable hydrogen atoms in their molecules. Thus hydrochloric acid HCl is a **monobasic acid**, sulphuric acid H_2SO_4 a **dibasic acid**, and phosphoric acid H_3PO_4 a **tribasic acid**. These terms relate to the fact that, in neutralization (see p. 258) the acids interact with one, two, or three molecules of a base like sodium hydroxide.

The Properties of Bases.—The properties of bases (p. 171) are properties of hydroxyl ion OH^-. A *base* is a substance which contains hydroxyl as a negative radical and, in solution, gives hydroxyl ion.

Many substances, such as ethyl alcohol C_2H_5OH, contain the hydroxyl group, but their solutions exhibit none of the characteristic properties of a base. They are not bases, since they do not contain hydroxyl as an ionizing radical.

A *strong base* is one which is highly ionized in solution, and therefore shows the properties of hydroxyl ion very markedly. It may be observed that the most active bases (alkalies) are the hydroxides of those metals (K, Na, Ba) which come first on the electromotive series (p. 240). *Weak bases*, like ammonium hydroxide and copper hydroxide, are little ionized in solution, and exhibit the properties of hydroxyl ion only feebly. Water is an exceedingly weak base.

Bases are also classified in a way similar to that described under acids: thus sodium hydroxide NaOH is a **monoacid base**, calcium hydroxide $Ca(OH)_2$ is a **diacid base**.

The Properties of Salts. — Salts are substances which contain a positive ionizing radical other than hydrogen, combined with a negative ionizing radical other than hydroxyl. The properties of a salt in solution are the properties of its two ions (see p. 226).

Salts like KCl and Na_2CO_3 are called **neutral** or **normal salts.** Salts containing a bivalent radical combined with two different univalent radicals, like $NaKCO_3$ and $Ca(OCl)Cl$ (bleaching powder) are **mixed salts.**

The most interesting classes of mixed salts are the **acid salts** and the **basic salts.** In acid salts, like $NaHSO_4$ (p. 162) and KH_2PO_4 (p. 412), only part of the available hydrogen of the acid has been replaced by a metal. In basic salts, like $Ca(OH)Cl$, part of the basic hydroxyl remains. The precipitate actually obtained by the action of a soluble carbonate on a cupric salt (p. 230) has the composition $Cu_2(OH)_2CO_3$. It is a *basic salt.*

There are also many cases in which salts combine together to form more complex **double salts**, like ferrous-ammonium sulphate

$(NH_4)_2SO_4,FeSO_4,6H_2O$, and alum (see index), some of which are in common use.

All these classes of salts are **electrolytes.**

Exercises. — 1. Which are the anions and which the cations in the substances whose formulæ are given on p. 222?

·2. Using the models given in p. 234, make the ionic equations representing the ionization of all the acids, bases, and salts, the formulæ of which are given on p. 222.

3. Make an ionic equation (p. 240) for the displacement: (a) of hydrogen from dilute hydrochloric acid by magnesium; and (b) of copper from cupric sulphate solution by zinc.

4. Rewrite the double decompositions on p. 224 in full ionic form.

5. Why does a solution of 0.1 N hydrochloric acid conduct the current nearly twice as well as a solution of 0.1 N sodium hydroxide, and nearly four times as well as a solution of 0.1 N sodium chloride?

6. From the results given on p. 228, calculate the degree of ionization of sodium chloride in a solution containing 1 gr. mol. wt. NaCl to 1000 g. water (a) at the boiling-point, and (b) at the freezing-point.

7. From the results given on p. 228, calculate the degree of ionization of potassium chloride in a solution containing 1 gr. mol. wt. KCl to 1000 g. water at 18°.

8. With solutions of the following substances, state (a) what will be the products of electrolysis, and (b) how they may be isolated in each case: Potassium chlorate, potassium chloride, silver sulphate, calcium hydroxide.

CHAPTER XVIII

IONIC EQUILIBRIA

Now that we have presented the main features of the ioniza-tion theory of Arrhenius, we shall proceed to amplify the argu-ment at certain points, in order to impress upon the student the primary importance of this theory and to accustom him to its use in chemistry by the consideration of some additional experi-mental illustrations. While studying these, we shall also take occasion to correlate ionic reactions with our *general laws of chemical equilibria*, as developed in Chapter XV. This topic will be treated mainly qualitatively here, the detailed quantita-tive discussion of ionic equilibria being left for a later chapter (pp. 566-578). Finally, we shall answer some of the objections which have been brought against the concept of ionization in solution, and return briefly to the significance of *valence*.

The Ionic Equilibrium with a Single Electrolyte. — In the ionization of a molecular substance, the chemical change is always incomplete and the system reaches a condition where the undissociated and the dissociated parts of the solute are in equilibrium (p. 234). The action is, therefore, reversible, and there are thus **two routes** to the same equilibrium point. This fact must not be forgotten, for we have to consider the union of ionic substances even more often than the converse change. Now, the **degrees of ionization** of various electrolytes **tell us** the location of the equilibrium point at any given concentration, and therefore **the extent of the chemical change** involved in reach-ing this point by *either route*, that is, either by the dissociation of molecules or by the union of ions. In a class of interactions, of which all are incomplete, and only those are interesting and useful which approach completeness, we require some means of knowing which are practically complete and why they are so.

The table of fractions ionized (p. 244) supplies most of the required information.

To illustrate, take the case of a single electrolyte. When we place hydrogen chloride in decinormal solution, 0.92 of the molecules dissociate. Conversely, when we start with the hydrogen-ion and chloride-ion, say by mixing two solutions, each of which contains one of them (along with another·ion), then 1 – 0.92, or only 0.08 of these ionic substances will combine.

ᴄ· This exemplifies the case of an active acid. The following equations show the data for six typical substances in $N/10$ solution, namely, two acids, two bases, and two salts:

(8%)HCl $\rightleftarrows$ H$^+$ + Cl$^-$(92%),   (98.7%)HC$_2$H$_3$O$_2$ $\rightleftarrows$ H$^+$ + C$_2$H$_3$O$_2^-$(1.3%)
(9%)KOH $\rightleftarrows$ K$^+$ + OH$^-$(91%),   (98.7%)NH$_4$OH $\rightleftarrows$ NH$_4^+$ + OH$^-$(1.3%)
(16%)NaCl $\rightleftarrows$ Na$^+$ + Cl$^-$(84%),   (60%)CuSO$_4$ $\rightleftarrows$ Cu^{++} + SO$_4^-$(40%)
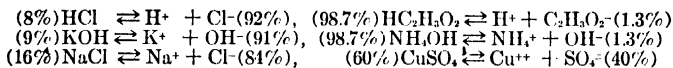
These samples are chosen to illustrate, in each pair, extreme cases. Thus, when potassium-ion and hydroxide-ion are brought together little union takes place, while with ammonium-ion and hydroxide-ion the union is practically complete. In the case of the soluble *salts*, however, there are almost (p. 244) no cases of considerable union of the ions in dilute solutions. The case of water, on the other hand, is one of the most extreme:

$$(>99.9\%) \ H_2O \rightleftarrows H^+ + OH^- \ (0.000,000,002\%).$$
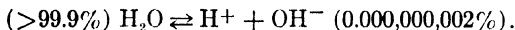
Hydroxide-ion and hydrogen-ion thus unite almost completely.

Similar reasoning enables us to handle the more complex, but very common case of the mixing of two electrolytes. The degrees of ionization tell us the exact condition of each system separately, before mixing. The result of the mixing is best understood by viewing the change as consisting in a *displacement* of each of the equilibria by the action of the components of the other. We consider, therefore, next, the displacement of ionic equilibria.

The Displacement of Ionic Equilibria. — Equilibria are displaced by changes which favor or disfavor one of the opposed actions (p. 208). There may be either, (1) a physical change in the conditions, or a chemical interaction which (2) adds to, or (3) removes one of the interacting substances. Each of these may be illustrated in turn.

As an example of the first, we have the **effect of changing the amount of the solvent** (p. 243). Adding more of the solvent reduces the concentration of the ionic materials and disfavors their union, so that it indirectly promotes dissociation. The larger the volume in which the ions are scattered, the less often will they meet, and the smaller the amount of combination. On the other hand, evaporating off a part of the solvent favors the encounters of the ions and promotes combination. When the solvent is at last entirely gone, the whole material is molecular.

In cases where the ionic and molecular substances are all colorless, these changes can be followed only by a study of the conductivities, freezing-points, or other similar properties of the solutions (p. 245). But when the substances are of different colors, the changes can also be seen. Thus, cupric bromide in the solid form is a jet black, shining, crystalline substance. When treated with a small amount of water it forms a solution which is of a deep reddish-brown tint, giving no hint of resemblance to a solution of any cupric salt. This doubtless represents the color of the molecules. When more water is added, the deep brown gives place gradually to green, and finally to blue. The latter is the color of the cupric-ion (Cu++), and is familiar in all solutions of cupric salts. The colorless nature of solutions of potassium and sodium bromides shows that bromide-ion (Br⁻) is without color. Hence, in the present instance it is invisible. We are thus watching the forward displacement of the equilibrium:

$$CuBr_2 \text{ (brown)} \leftrightarrows Cu^{++} \text{ (blue)} + 2Br^{-}.$$

If we now remove the water by evaporation, all these changes are reversed. When the water is all gone, the black residue remains. Here we are observing the backward displacement of the equilibrium, $CuBr_2 \leftrightarrows Cu^{++} + 2Br^{-}$.

Illustration by Means of Conductivity Measurements. — Observation of the changes in the conductivity of a solution, when the concentration is altered, supplies another simple and more general means of studying the displacement of ionic equilibria.

A glass trough and ammeter * (Fig. 75) may be used to illustrate this principle. The electrodes are long strips of copper foil, which pass down at the ends of the trough. After placing the two instruments in circuit with a source of electricity, we first pour very pure water into the cell. With this arrangement, the ammeter does not indicate the passage of any measurable current of electricity. Concentrated (36 per cent) hydrochloric acid is next cautiously added through a long-stemmed dropping funnel, so that it forms a shallow layer below the water, and the funnel is withdrawn. The situation at this stage is that a definite amount of hydrogen chloride dissolved in a *small* amount of water fills what was before practically a nonconducting gap
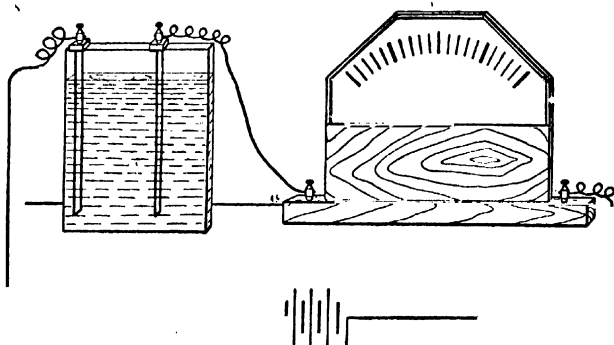
Fig. 75'

in the electric circuit. The deflection of the needle in the ammeter indicates that a feeble current is now able to pass through the circuit. When, however, we stir the surface of the acid very gently with a thin glass rod, the ammeter instantly responds, showing a large increase in conductivity. As we stir, the conductivity increases, and the increase ceases only when the liquid has become homogeneous. Introduction of an additional supply of water will improve the conductivity still more, but

* An ammeter (ampere-meter, see p. 237) is an instrument by means of which the number of coulombs of electricity passing through the solution per second is indicated. In the above experiment, an ammeter of low resistance must be used.

the effect becomes less and less, until no change on further dilution is perceptible. Reasoning about these effects, we perceive that the *amount* of hydrochloric acid has not altered during the experiment. Yet the quantity of conducting material between the electrodes must have become greater, for the carrying power of the whole has improved. We were therefore observing the progress of a chemical change of the nonconducting hydrogen chloride into conducting hydrogen ions and chloride ions. Furthermore, the change practically ceased at great dilution, for the dissociation into ions was then practically complete. If we could conveniently have started with only liquefied, dry hydrogen chloride in the cell, we should have observed the whole range of changes from zero to the maximum.

When a very concentrated solution of cupric chloride is used instead of hydrochloric acid, dilution is accompanied by a similar improvement in conductivity. Here we notice, besides, that the yellowish-green liquid, with which we start, changes to a pale blue, as the yellowish-brown molecules of cupric chloride are dissociated and the color of the solution becomes more exclusively that of the copper ions. When the solution has become perfectly blue, further dilution is seen to affect the conductivity but slightly.

Other Methods of Displacing Ionic Equilibria. — Cupric bromide may be used to illustrate also the chemical methods of displacing equilibria. Thus, we may show the **effect of adding more of one of the reacting substances.** If, at the green stage, we dissolve solid potassium bromide in the liquid ($KBr \rightleftarrows K^+ + Br^-$), the increased concentration of bromide-ion causes more vigorous interaction of the ions, and the molecules, with their brown color, become prominent again. Adding cupric chloride increases the concentration of cupric-ion and has the same effect. In either case, renewed dilution with water reduces the concentrations of all the ions once more, the molecules become fewer, and the brown color is displaced by the blue for the second time.

Finally, the displacement of the same equilibrium **by removing one of the interacting substances** may be illustrated. Thus, if the chocolate-brown solution, in which molecular cupric bromide

predominates, is shaken with pulverized lead nitrate (and fil-
tered), two changes are noticed. A pale yellow precipitate of lead
bromide appears $(Pb^{++} + 2Br^- \rightarrow PbBr_2 \downarrow)$, and the *brown
color fades into green.* Here the displacement is the opposite of
the last. Instead of reinforcing one of the ions, we have reduced
the concentration, and in fact almost entirely removed one of
them, namely Br^-. This has, naturally, stopped the interaction
of the $Cu^{+,+}$ and Br^- which reproduces the brown, molecular
$CuBr_2$. Hence the dissociation of the latter has continued to
exhaustion of the whole molecular material.

The color changes discussed on p. 209 in connection with the
reaction $FeCl_3 + 3NH_4.CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl$ also illus-
trate this point. The red color is due entirely to undissociated
ferric thiocyanate. The reader should re-examine this equi-
librium carefully, writing the equation in full ionic form. He
will then be in a position to understand why the addition of *any*
ferric salt or of *any* thiocyanate to a given mixture will deepen
the red color, while the addition of *any* chloride (except ferric
chloride) or *any* ammonium salt (except ammonium thiocyanate)
will tend to lighten it.

The reader will find that the behavior of these ionic equilibria,
and the way in which we discuss and explain it, are complete
parallels of the behavior and explanation in the case of ordinary
equilibria (pp. 213-214). The illustrations in the present section,
and particularly the last, should be considered until every feature
is perfectly clear. They furnish the key to understanding the
applications which follow. One fact must not escape notice,
and that is that in none of the three instances was the forward
action (the dissociation) in itself affected. The molecules of
cupric bromide have, as we should expect, a certain tendency to
decompose. No encounters between these molecules are required
for mere decomposition. Hence their decomposition is not in-
fluenced by their nearness to, or remoteness from, one another,
nor by the presence of any other kinds of molecules or ions. The
effect, whether it involved an apparent increase, or a diminu-
tion of the dissociation, *was always accomplished by altering the
concentration of the ionic substances, and therefore the activity
of the reverse action.*

Double Decomposition in Solution. — We are now prepared to consider more closely the general case of mixing the solutions of *two* electrolytes.

When solutions of two ionized substances are mixed, the first reflection which occurs to us is that each of these has been diluted by the water in which the other was dissolved, so that the first effect will be to increase the degree of ionization of both to a certain extent. If solutions already very dilute are used, however, this effect will be negligible.

The next consideration is, however, that we have produced a mixture of four ions, which must have at least some tendency to unite crosswise. Thus potassium chloride and sodium nitrate in dilute solution are very greatly ionized before mixing. The reversible actions, represented by the horizontal pair of the following equations, have taken place extensively. But, by mixing the liquids, we have brought into presence of one another two new pairs of positive and negative ions. Hence, two other reversible actions, the vertical ones, will be set up and will proceed until a fresh equilibrium of all the ions with all four kinds of molecules has been reached. Thus far the description will fit any case of mixing solutions of two electrolytes.
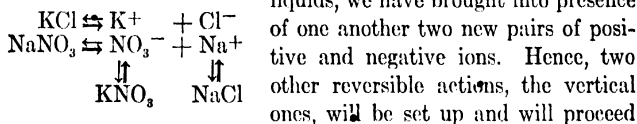
$$\begin{array}{ll} KCl \rightleftharpoons K^+ & + Cl^- \\ NaNO_3 \rightleftharpoons NO_3^- & + Na^+ \\ \quad \Updownarrow & \quad \Updownarrow \\ KNO_3 & NaCl \end{array}$$

Now, in this particular instance, what is the actual extent of such interaction as has occurred? To answer this question we require to know the proportion of molecules to ions in a solution of each of the four salts (p. 244). In decinormal solutions it is KCl, 14 : 86; NaNO$_3$, 17 : 83; KNO$_3$, 17 : 83, NaCl, 16 : 84, so that the salts are all equally well ionized. It is a good plan to add these proportions in the formulation. Furthermore, in a *very dilute* mixture, such as we are considering, the *proportions of ions are greater than these figures indicate.* Hence, very little chemical action has actually occurred.

$$\begin{array}{ll} & (> 83\%) \quad\quad (> 84\%) \\ (14\%)\, KCl \rightleftharpoons K^+ & + \quad Cl^- \ (86\%) \\ (17\%)\, NaNO_3 \rightleftharpoons NO_3^- & + \quad Na^+ \ (83\%) \\ \quad\quad \Updownarrow & \quad\quad \Updownarrow \\ \quad\quad KNO_3 & \quad\quad NaCl \\ \quad\quad (< 17\%) & \quad\quad (< 16\%) \end{array}$$
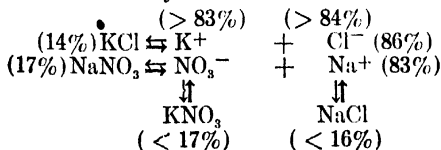
That this inference is correct is shown by independent evidence. Thus when the solutions of salts are mixed, **no thermal effect** is observable. This fact has been known since **1842** as Hess' **law of thermoneutrality.** Again, if the solutions are placed in a cell (Fig. 75, p. 252), so that the one forms a layer below the other, no appreciable change in conductivity is noticed when the solutions are stirred together. Hence no significant change in the number of ions has occurred.

'" We conclude, then, that when two highly ionized substances are mixed, **and the possible products are also highly ionized, soluble substances,** then **very little chemical action occurs.** This rule applies to dilute solutions of all soluble salts (p. 244) and to mixtures of salts with the highly ionized acids or bases.

Conversely, when two ionized substances are mixed, **an extensive chemical change does ensue in two cases,** namely:

1. When one of the possible products is an insoluble substance and **precipitation** occurs, for this removes the ions used to form the insoluble body.

2. When one of the possible products, although soluble, is **little ionized,** for this likewise removes the ions required to form molecules of the product. We proceed, therefore, to discuss these two important classes of actions.

. **Precipitation.** — A typical case of precipitation, which occurs when we mix dilute solutions of silver nitrate and hydrochloric acid, has already been discussed in some detail (pp. 241-242). A still more striking example, the interaction of silver sulphate and barium chloride in solution, is analyzed briefly below.

$$
\begin{array}{ccc}
(>99\%) & (>99\%) \\
(30\%)\ \mathrm{Ag_2SO_4} \rightleftharpoons 2\mathrm{Ag^+} & + & \mathrm{SO_4} = (70\%) \\
(24\%)\ \mathrm{BaCl_2} \rightleftharpoons 2\mathrm{Cl^-} & + & \mathrm{Ba^{++}}\ (76\%) \\
\qquad \updownarrow & & \updownarrow \\
\text{(dissolved) } 2\mathrm{AgCl} & & \mathrm{BaSO_4}\ \text{(dissolved)} \\
\qquad \updownarrow & & \updownarrow \\
\text{(solid) } 2\mathrm{AgCl} & & \mathrm{BaSO_4}\ \text{(solid)}
\end{array}
$$
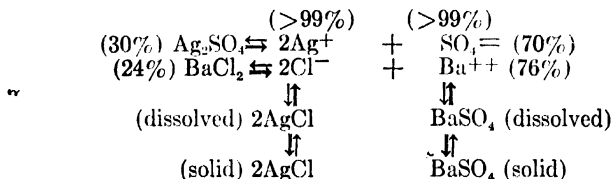
Here, since the four undissociated substances are all salts, they are all highly ionized in solution. If they were all soluble, then, in say one-twentieth normal solution, perhaps about 20

per cent of each salt would be in the molecular condition and the rest in ionic form. But *the molecules of silver chloride and of barium sulphate are both excessively insoluble.* If we refer to the Table of Solubilities inside the front cover (*which we should do in studying all cases of precipitation*) we find that one liter of water at 18° will dissolve only 0.0016 g. of silver chloride and only 0.0022 g. of barium sulphate. These quantities include *both* ions and molecules. **So far as the salts are in solution, however, being salts and exceedingly dilute, they are practically entirely ionized.** Hence the concentrations of undissociated AgCl and BaSO₄ in solution are almost zero. As fast as Ag⁺ and Cl⁻, or Ba⁺⁺ and SO₄⁼, combine in the mixed solutions of Ag₂SO₄ and BaCl₂, therefore, AgCl and BaSO₄ are precipitated, and the four ions almost disappear. This occurrence affects in turn the undissociated Ag₂SO₄ and BaCl₂, which continue to ionize until they are completely eliminated. Hence we are left at last, if we use equal volumes of equivalent solutions, with a mixed precipitate of silver chloride and barium sulphate, and a solution which is practically pure water.

This experiment may also be carried out in the apparatus shown in Fig. 75 (p. 252). The silver sulphate solution is first introduced into the cell, and an equivalent quantity of barium chloride solution, weighted with sugar to increase its density and prevent mixing, is carefully run in beneath it by means of a funnel. (It is preferable to separate the two solutions altogether by running a little pure sugar solution through the funnel before adding the barium chloride.) When the current is turned on, the ammeter indicates that the two solutions, before mixing, possess considerable conductivity. After the solutions are thoroughly mixed by stirring, the pointer drops back practically to zero.

To avoid a misconception, note that the answer to the question, "Is silver chloride a highly ionized substance in solution?" is "Yes." Since it is a salt, we expect this. True, very little of it dissolves, so that it cannot give many ions to a solution (see p. 227). But little or much ionized refers to the proportion ionized of the material which *has* dissolved. With undissolved material ionization has nothing to do.

Returning now to our previous example of silver nitrate and hydrochloric acid (p. 241), it should be noted that, when the solutions are mixed, strictly speaking, the main *interaction* taking place is the production of the *insoluble body.* The largest part of the chemical action may be formulated thus:

$$Ag^+ + Cl^- \rightarrow AgCl.$$
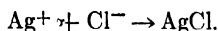
The chief change that has as yet befallen the ions of nitric acid is that they have been transferred from two separate vessels into one. Potentially the acid has been formed. But the actual union of its ions, to give the second product in the molecular condition,

$$H^+ + NO_3^- \rightarrow HNO_3,$$
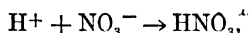
comes about quantitatively only when, at some subsequent time, if at all, the water is evaporated away.

The foregoing formulation and explanation apply to every case of mixing ionogens where precipitation occurs, that is, where the products are insoluble acids, bases, or salts. That precipitation, however, is *never absolutely complete* is an important point, the consequences of which will be examined in detail in a later chapter (pp. 569-578).

Neutralization. — We may now consider the case of **mixing solutions of two ionogens** where one is **an acid** and one **a base.**

The general plan of all interactions of acids and bases is shown in the formulation. The ionization of the hydrochloric acid reaches 0.92 in a decinormal solution, and goes farther when the acid is diluted with the water of another solution. That of the sodium hydroxide similarly goes beyond 0.91. Thus the substances in the solutions before mixing are almost entirely ionic. The crosswise union, $H^+ + OH^- \leftrightarrows H_2O$, however, is all but complete, for water is hardly ionized at all (p. 245). The

$$
\begin{array}{cc}
(> 84\%) & (< 0.01\%) \\
(8\%)\ HCl \leftrightarrows Cl^- & +\ H^+\ (92\%) \\
(9\%)\ NaOH \leftrightarrows Na^+ & +\ OH^-\ (91\%) \\
\text{\Updownarrow} & \text{\Updownarrow} \\
NaCl & H_2O \\
(< 16\%) & (100\%)
\end{array}
$$

materials on whose interaction with the Cl⁻ and Na⁺, respectively, the maintenance of the molecules HCl and NaOH depends, being thus removed, the dissociation of the acid and base promptly brings itself to completion, and the left sides of the equations vanish. Practically all the hydrogen-ions and hydroxide-ions become water, which thenceforth is simply a part of the solvent. The Cl⁻ and Na⁺, however, if the solution is decinormal, unite to the extent of 0.16 only. Since it is more dilute, this union forms a still smaller factor in the whole change. Practically it is negligible. Now all that has been said of *this* acid and base will apply (changing the names of the ions of the salt) whenever any active, highly ionized acid and base come together. Thus we may write **one simple equation for all neutralizations of active acids and bases:**

$$H^+ + OH^- \rightarrow H_2O.$$
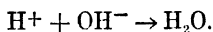
without omitting anything essential.

The ions of a salt are always left over from the main action, and may be brought together, in turn, by evaporation: Na⁺ + Cl⁻ → NaCl, or the liquid may be used as a solution of the pure salt.

Confirmations of this View of Neutralization. — That these

inferences are correct is shown by many facts. The most conspicuous of these is the fact that, when *equivalent* amounts of *active* acids and bases are used, the mixture is *without action* either *on red or on blue litmus.* It is **neutral** to indicators — hence the term **neutralization** applied to the operation of mixing an acid and a base. Specifically, the absence of effect upon litmus demonstrates the absence of hydrogen-ion H⁺ and of hydroxide-ion OH⁻, alike, in the product, and confirms the theory.

Again, a considerable thermal effect accompanies neutralization. But, in the cases we are discussing, that is where *active* bases and acids are employed, the heat liberated by use of equivalent weights (p. 142) is *always the same,* namely **13,700 calories.** That it is always the same confirms our theory, for

practically the whole change is always the formation of **18.016 g.** of water from the ions.

Still again, when we place the acid and base in the cell (Fig. 75, p. 252), so that the one forms a layer beneath the other, and watch the ammeter while we mix the solutions, a marked *decrease* in the current passing through the cell is noticed. This also confirms our theory, for it is our belief that one-half of the ions, namely the H+ and OH⁻, disappear as such during the action. The decrease is, in fact, to less than half the reading before mixing, because the two speediest ions have been removed.

When rather less highly ionized acids or bases are used, the only difference is that there are more of the molecular materials present, before the solutions are mixed. But the removal of the H+ and OH⁻ ions permits the molecules of the acid and base to dissociate, so that the final products are water and the ions of a salt, as before. When either the acid or the base employed is *very weak*, however, the tendency of water to break up into H+ and OH⁻ must be taken into consideration (see hydrolysis, p. 324).

The foregoing formulation and explanation apply to every case of mixing ionogens, where a very slightly ionized substance is one of the products, that is, when water, or a feeble acid, or a feeble base (p. 245) is formed. We may note that this is a **third method** (compare p. 215) of **driving a reversible reaction practically to completion**, which is very frequently utilized by chemists in carrying out reactions.

Acidimetry and Alkalimetry. — When, as is constantly the case, a chemist desires to ascertain the **quantity** of an acid or base present in a solution, he uses for the purpose the interaction just discussed. If, for example, the problem is to ascertain the weight of hydrogen chloride in each liter of a specimen of hydrochloric acid, this can be done by neutralizing a measured portion of this acid with a solution of an alkali of *known concentration*. The volume of the latter which is required for the purpose is observed. If the alkali is sodium hydroxide, the action taking place is

$$HCl + NaOH \rightarrow H_2O + NaCl.$$
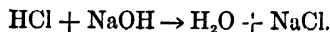
The volume of acid is measured out into a beaker by means of a pipette (Fig. 76) of fixed capacity, which is filled by suction to the mark on the stem. Suppose the amount to be 25 cc. The standard alkali solution is placed in a burette (Fig. 77), which is filled down to the tip of the nozzle. A few drops of litmus so-lution are now added to the acid, and the alkali is allowed to run in slowly. After a time, the hydroxide-ion which this introduces will begin to produce a blue color, close to where the stream en-ters the liquid. This is at first dissipated by stirring, and the whole remains red. Finally, however, a point is reached at which the entire solution assumes a tint intermediate be-tween blue and red.
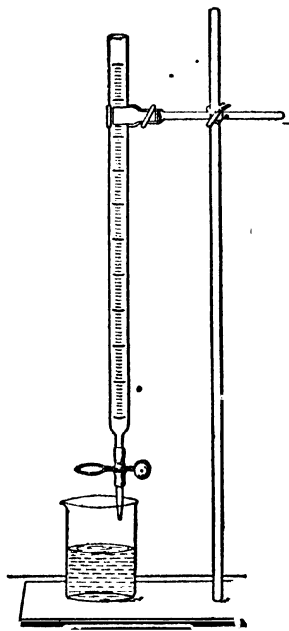
FIG. 76.   FIG. 77.

With one drop less of the base, it is distinctly red. With one drop more, it would become distinctly blue. Litmus paper of either shade dipped in this neutral solution remains unaffected.

By the use of a standard solution of an acid in the burette, the quantity of a base may be determined in the same way.

Standard Solutions. — The **standard solutions** used in this work are usually normal, and contain one equivalent weight of the alkali or acid in one liter of the solution. For more delicate

work, decinormal (N/10) solutions may be employed. The concentration of such a solution is called its **titer**, and the operation of analyzing another solution by means of it, **titration**. The value of standard solutions lies in the fact that, when once the solution has been prepared, and the exact concentration adjusted by quantitative experiments, its use does not require any weighing, and the measurements of volumes can be carried out with great rapidity.

The calculation of the result is also simple. One liter of normal alkali contains 17.008 g. of available hydroxyl, and one liter of normal acid, 1.008 g. of available hydrogen (p. 142). Equal volumes of normal solutions will therefore exactly neutralize one another, 18.016 g. of water being formed by interaction of a liter of each. If, for the neutralization of the 25 c.c. of hydrochloric acid used above, 50 c.c. of normal alkali are required, the acid is twice-normal (2 N). When 15 c.c. are required, the acid is $^{15}\!/_{25}$ or $\frac{3}{5}N$. If the actual weight of the acid in the latter case has to be calculated, we remember that there are 36.468 g. of hydrogen chloride in 1 l. of a normal solution, and therefore $36.468 \times \frac{3}{5} \times {}^{25}\!/_{1000}$ g. $= 0.5469$ g. in 25 c.c. of a solution which is $\frac{3}{5}$-normal.

Methods of quantitative analysis in which standard solutions are employed are known as **volumetric** methods, and are much used by analysts and investigators. They occupy much less time than **gravimetric** operations, in which numerous weighings have to be made, and are often just as accurate. The substances, like litmus, by whose change of color the completeness of the action is made known, are called *indicators*.

Indicators. — Indicators are substances which, in presence of certain other substances, assume a very deep color, or change sharply from one deep color to another. Thus, **phenolphthalein** (see p. 239) is colorless in presence of acids (*i.e.*, hydrogen-ion), and red (when dilute, pink) in presence of alkalies (*i.e.*, hydroxide-ion). **Litmus**, again, is red with acids, and blue with alkalies. The change of color depends upon a chemical interaction in each case, but since indicators are chosen for their strong coloration, the quantity of the acid or base used up in

changing the tint of the trace of the indicator is so small as to be negligible. Other common indicators are **Methyl orange**, a complex organic compound which gives, in acid solution, a red, and in alkaline solution a yellow color, and **Congo red**, the sodium salt of an acid of complex structure (see Dyes). In neutral or alkaline solutions this is red; with acids it turns blue. Paper dipped in Congo red differs from litmus paper in that it shows gradations in color, the blue being much more distinct with an active acid than with a relatively weak one like acetic acid (p. 245). Litmus paper is equally red with all acids save the very feeblest.

The Part Played by the Solvent in Ionization. — So far, we have regarded water as playing merely a physical rôle in the ionization of electrolytes. The ions in a solution of hydrogen chloride, for example, have been regarded as H^+ and Cl^-, the solvent breaking up the molecule HCl in some way, but not being itself directly concerned in the reaction.

This view, although sufficient for many purposes, will not stand strict investigation. Thus we know by experiment that the ions, when they migrate with the electric current in electrolysis, carry water with them. This indicates that ions are *hydrated*. The solvent is therefore *chemically active* in ionization.

Recent work, indeed, suggests that the distinction drawn between solvent and solute in explaining ionization phenomena is entirely misleading. Pure liquefied hydrogen chloride is practically a non-conductor, just like pure water. It is quite an arbitrary procedure, therefore, to ascribe all of the conducting power of a mixture of hydrogen chloride and water to the former substance, and to regard the latter as quite inert. It would be more logical to consider both components of the solution as equally concerned in ionization. Now experiment shows that extensive *ionization* in solution always accompanies extensive *compound formation* on admixture. When no interaction at all between the components occurs, the solution is non-conducting. All strong acids, for example, give hydrates with water which are sufficiently stable to be isolated in the solid state. No very

weak acids give isolable hydrates. Those mercuric salts which are highly ionized, as mercuric nitrate $Hg(NO_3)_2$, all yield hydrates, such as $Hg(NO_3)_2,8H_2O$. Those which are only slightly ionized are all non-hydrated. It is possible, therefore, to regard ionization as due to the formation of solvent-solute complexes. The attractive forces between the constituent groups in such complexes would be considerably weaker than in the simpler molecules of the two components, and disintegration into oppositely-charged radicals could occur much more readily.

It should be added that ionization is not restricted to solutions of electrolytes in *water*. Many other solvents, such as liquid ammonia NH_3, formic acid $H.COOH$, ethyl alcohol C_2H_4OH, dissolve many electrolytes to give solutions of excellent conducting power. Water, however, is the solvent most commonly used in chemical operations, and other ionizing solvents need not be considered at this stage.

Some Possible Misunderstandings. — Before we close the chapter, it will be profitable to anticipate some difficulties into which the reader may fall. If the ionic hypothesis is not properly understood, it appears to conflict so strongly with what the student has learned in previous chapters that he is apt to become hopelessly confused. The following points of possible misunderstanding and the explanations appended should therefore be read through very carefully. For convenience of illustration, *sodium chloride* is taken as a typical electrolyte in the questions and answers listed below. The student should test his knowledge of the subject by substituting other electrolytes.

1. If sodium chloride is broken up in aqueous solution into *sodium* and *chlorine,* why do we not find any of the properties of sodium or of chlorine exhibited by the solution? — This has always been a very common misapprehension of the ionic theory. Many prominent chemists never could understand how sodium (a *metal* which acts vigorously on water) and chlorine (an obnoxious *gas*) could exist side by side in a solution of sodium chloride without immediately notifying us of their presence by characteristic reactions. The answer is that *free sodium* and *free chlorine* do *not* exist in sodium chloride solution. The ionic

hypothesis has never stated that they do. What it does state is that *sodium ion* Na⁺ and *chloride ion* Cl⁻ are present in the solution. These are *entirely different substances* from atomic sodium Na and molecular chlorine Cl₂. The electric charges on the ions change their properties completely. There is no more reason why they should behave like free sodium and free chlorine than there is for crystals of common salt to behave like a *mixture* of sodium and of chlorine. Metallic sodium Na reacts with water to form a solution of sodium hydroxide. In sodium chloride solution, however, the ionic sodium Na⁺ is *already* in the same state as it is in sodium hydroxide solution, and is in no need of trying to enter that state.

2. Salt is a very stable substance. The union of sodium and chlorine evolves a great deal of heat. A great deal of work will be required, therefore, to decompose sodium chloride. How can mere addition of water break it up? — We have here the same misunderstanding in another form. It is true that it would be very difficult to decompose sodium chloride into *free sodium* and *free chlorine*, but its dissociation into *sodium ion* and *chloride ion* is an entirely different question. As a matter of fact, the heat of ionization is extremely small. Sodium chloride is stable only in a solid state. In solution, it reacts with very great facility with many other electrolytes.

3. Why do not the ions Na⁺ and Cl⁻ *recombine at once*, in response to the attractions of their charges? — The answer is that they do combine. The tendency towards combination is, however, opposed by the tendency of undissociated NaCl to decompose into *free ions*. An equilibrium between the two tendencies is, therefore, set up, which we may express by the reversible reaction $NaCl \rightleftarrows Na^+ + Cl^-$.

4. Why can we not separate sodium ions from chloride ions in a solution of sodium chloride *before* we pass a current through the solution? Does not this show that it is the electric current which breaks up the sodium chloride? — The charges on the ions are *not* derived from the electric current. Free sodium ions and free chloride ions are present in the solution the instant the salt is dissolved, whether a current is passing or not. Before we pass a current through the solution, however, any portion of it

of sensible magnitude contains just as many sodium ions as chloride ions. By making use of the fact that the chloride ion *diffuses* more rapidly than the sodium ion (into a layer of pure water, for example, carefully poured over the solution) we can bring about a slight separation of the two ions, the water layer becoming negatively charged and the solution positively. The passage of the current does not *cause* ionization, it merely makes its existence more obvious, effectually separating the ions by forcing them to migrate in different directions towards the oppositely-charged electrodes.

Ions and Electrons. — The question may be asked: Whence *do* the ions obtain their electric charges? A brief answer to this question may be attempted here, although for a clear realization of its significance a knowledge of the subject-matter of the final chapter (pp. 729-731) is necessary.

Matter is electrical in its ultimate nature, and the atoms of all elements are more or less complex aggregates of positive and negative electrical units. The positive units (*protons*) constitute the main mass of the core or nucleus of the atom, and are *fixed* therein, except in radioactive disintegrations. The outermost shell of the atom consists of a number of negative units (*electrons*), which are less rigidly held. The atom as a whole, of course, is electrically neutral. The hydrogen atom, to choose the simplest example, is made up of a single proton and a single electron. The structure of the atoms of other elements is, of course, more complex, but all possess, in their outermost shell, a definite small number of electrons, which are relatively loosely held. When two atoms of different elements *combine*, it may happen that an electron (or a number of electrons) will pass from one atom to the other. Atoms which lose electrons in this way become positive radicals, the departure of an electron leaving the atom as a whole electrically *positive*. Atoms which *gain* electrons become *negative* radicals, arrival of an electron making the atom as a whole electrically *negative*. Under normal circumstances, the attractive forces between such oppositely-charged radicals will be sufficient, in most cases, to bind them firmly together as *electrically neutral*

molecules. If we *weaken* these forces, however, as we undoubtedly do when we dissolve an electrolyte in a solvent such as water, separation of the *bound radicals* into *free positive and negative ions* can be effected much more readily, and extensive ionization may result.

A *positive ion,* therefore, is a free atom which has *lost* an electron, or a number of electrons, such as Na+, (NH₄)+, Zn++. A *negative ion* is a free atom, or group of atoms, which has *gained* an electron, or a number of electrons, such as Cl⁻, (NO₃)⁻, S⁼.

Reconsidering now the section on **ions and displacement** (p. 240), we see that **the electromotive series of the metals represents the order of the tendency of the free elements to lose electrons.** The higher a metal stands in this series, the more readily will its atoms assume the ionic state by transference of electrons to positive ions of metals lower down in the series. If we represent an **equivalent of electrons** (the quantity of electricity carried by one equivalent of a negative ion) by ⊖, therefore, we can write the action of zinc on a solution of a copper salt as the result of two concurrent reactions:

$$Zn \rightarrow Zn^{++} + 2\ominus; \quad 2\ominus + Cu^{++} \rightarrow Cu.$$
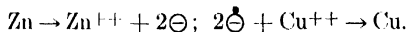
Similarly for the action of aluminium on hydrochloric acid (p. 127):

$$2Al \rightarrow 2Al^{+++} + 6\ominus; \quad 6\ominus + 6H^{+} \rightarrow 3H_{2}.$$
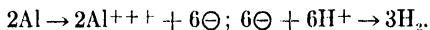
Valence and Electrons. — On the basis of electrons, our idea of valence becomes somewhat more definite. The valence of an element is the *number of electrons that an atom of that element loses, or takes up, in entering into combination with atoms of other elements.* An atom of hydrogen has only one electron to lose, the hydrogen ion H+ consists of nothing but the residual proton. Consequently hydrogen is univalent. An atom of Zn, however, can lose two electrons to form Zn++, and an atom of Al can lose three to give Al+++. An atom of Cl can gain one electron to form Cl⁻, an atom of S can gain two to give S⁼.

The relation of valence to atomic structure in the case of these and other elements will be taken up in detail in the final chapter.

A List of Valences and Charges. — The following table presents, for the guidance of the student, the valences of some familiar ions and the *commonest* valences of some elements. Many of these elements, however, possess other regular valences, in addition to those shown, so that the list does not pretend to be complete.

Univalent	Bivalent	Trivalent	Quadrivalent
Na-	Ca++	Al+++	Sn++++ (stannic)
K+	Ba++	Fe+++ (ferric)	(SiO₄)==
H+	Mg++	Cr+++	C (CH₄, CO₂)
(NH₄)+	Zn++	Sb+++	
Ag+	Pb++	Bi+++	**Quinquivalent**
Cl-	Ni++	(PO₄)≡	
Br-	Co++	As (AsH₃)	N (N₂O₅)
I-	Mn++	B (B₂O₃)	P (P₂O₅)
F-	Cu++ (cupric)	N (NH₃, N₂O₃)	As (As₂O₅)
(OH)-	Fe++ (ferrous)	P (PH₃)	
(NO₃)-	Hg++ (mercuric)		**Sexivalent**
(ClO₃)-	Sn++ (stannous)		
	O-		S (SO₃)
	(SO₄)=		
	S=		
	(CO₃)=		
	O₂= (peroxide)		

Where no charges are indicated, the element, by itself, does not ordinarily form an ion.

Exercises. — 1. In the case of the chocolate-brown, concentrated solution of cupric bromide (p. 251), explain in detail what would happen to the system: (*a*) if metallic zinc were to be added (p. 240); (*b*) if hydrogen sulphide gas were to be led into the solution (CuS is insoluble).

2. Formulate, after the models on p. 255, and discuss fully, the interaction of ferric chloride and ammonium thiocyanate (p. 209).

3. For the neutralization of 77 c.c. of a certain alkaline solution, 25 c.c. of normal hydrochloric acid are required. What is the concentration of the alkali (p. 262)? If the alkali was sodium hydroxide, what weight of the substance was present? If the alkali was barium hydroxide, what weight of it was present?

4. What would be the conductivity change in experiments similar to that discussed in the case of silver sulphate and barium chloride solutions on p. 256, in which the two solutions to be mixed were: (a) hydrochloric acid and sodium acetate in equivalent quantities, (b) acetic acid and ammonium hydroxide in equivalent quantities, (c) ammonium chloride and sodium hydroxide in equivalent quantities? Formulate the ionic equilibria in detail first in each case, and then set down more briefly, as on p. 258, the essential changes that occur on admixture.

5. A normal solution of hydrochloric acid is 78 per cent ionized; a decinormal solution is 92 per cent ionized. Which of the two solutions, when filling the glass trough in the apparatus shown in Fig. 75 (p. 252), will show the greater conductivity? Reconcile your answer with the results obtained on pp. 252-253.

CHAPTER XIX

THE HALOGEN FAMILY

THE elements, if we may judge from those studied or mentioned thus far, may be divided into two classes — the metallic or positive elements, like sodium, zinc and magnesium, and the non-metallic or negative elements, like oxygen, chlorine and sulphur. The former give positive ions, such as Na^+, Mg^{++}. The latter give negative ions, such as Cl^-, $S^=$. Hydrogen constitutes the single exception, giving the *positive* ion H^+.

Natural Families of Elements. — We have a simple means of subdividing *within* each of these two classes. We can place together the elements of like chemical behavior. Thus, among univalent positive elements, sodium and potassium, and, among bivalent positive elements, zinc and magnesium resemble one another very closely in their reactions. Also, oxygen and sulphur form one group and chlorine, bromine, iodine and fluorine form another. Groups of this kind are often spoken of as **natural families** of elements. The last group is called the **halogen family,** from the Greek for *salt-producing*, because these elements combine with sodium to give substances all resembling common salt. Usually, the elements of one family and their corresponding compounds resemble one another in a number of ways, and show at the same time a gradation in properties which it is interesting to study.

BROMINE Br_2

The element was discovered by Balard in 1826 and derives its name from its offensive odor (Greek, *a stench*).

Preparation. — The salt deposits and natural salt wells of Cheshire, of Germany, and of Michigan, West Virginia, Ohio, and Connecticut, contain some bromides, along with large quantities of common salt. When the latter has been largely separated by

evaporation and crystallization, the bromides of sodium and magnesium, which are more soluble, collect in the mother liquor.

The bromine can be liberated at the positive electrode by electrolysis. But usually a chemical process is employed.

In one process, chlorine gas is dissolved in the liquor. This displaces the bromine, and the latter can be distilled out by heating:

$$2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2.$$
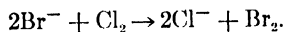
In another process, oxidation of a bromide by pulverized manganese dioxide and sulphuric acid is employed, and this method can be used in the laboratory (Fig. 78).
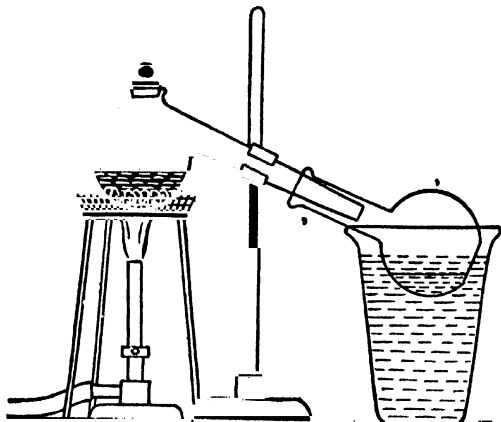
FIG. 78.

The manganese dioxide is reduced to manganous sulphate (compare p. 178), its oxygen combining with hydrogen from H_2SO_4 to form water. The sodium bromide used is converted to sodium hydrogen sulphate (compare p. 162) and bromine is liberated.

Skeleton: $NaBr + MnO_2 + H_2SO_4 \rightarrow Br_2 + NaHSO_4 + MnSO_4 + H_2O.$

Balanced: $2NaBr + MnO_2 + 3H_2SO_4 \rightarrow Br_2 + 2NaHSO_4 + MnSO_4 + 2H_2O.$
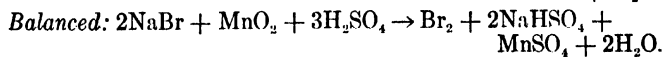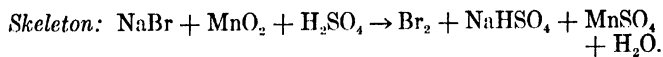
The beginner will doubtless find it difficult to balance the above equation by himself, since the method formerly recommended (p. 113) is not readily adapted to reactions in which several initial substances or products are involved, particularly when (as happens in this case) changes of valence on the part of certain elements also occurs in the course of the reaction. Rules for his assistance in working out this and similar complex equations will be presented in the following chapter.

Physical Properties. — Bromine is a liquid of a deep red-brown *color* and the vapor, of the same color, has a suffocating *odor*. It *boils* at 59°, forming a dark-red vapor, and even at ordinary temperatures gives a high vapor pressure (150 mm. at 18°) and evaporates quickly when exposed to the air. When cooled it forms red, needle-shaped crystals, which *melt* at − 7.3°. It is moderately *soluble* in water, giving a 3.2 per cent solution (**bromine-water**), and is very soluble in carbon disulphide. The *density* of the vapor gives it the formula Br_2.

Great care must be used in handling bromine, as, when spilt upon the skin, it kills the tissues and the sore is very liable to become infected. Burns made by bromine or concentrated acids should be washed instantly with water and then with bicarbonate of soda solution, and covered thickly with vaseline, or a salve of boric acid in lanoline, to protect them from infection.

Chemical Properties. — A jet of burning *hydrogen* will continue to burn in bromine vapor, giving hydrogen bromide, a gas which fumes in moist air like hydrogen chloride:

$$H_2 + Br_2 \rightarrow 2HBr.$$
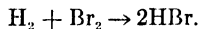
Many of the *metals*, when thrown in the form of powder, leaf, or foil, into bromine vapor, combine directly, giving bromides. The action is similar to that with chlorine, but less vigorous. Some of the non-metals, like phosphorus and arsenic, also burn in bromine vapor.

Hydrogen Bromide HBr, Preparation. — Hydrogen and bromine vapor unite much less readily than hydrogen and chlorine. A stream of pure hydrogen bromide is most easily made by

moistening red phosphorus with water, and allowing bromine to fall drop by drop into the paste (Fig. 79). To absorb the bromine vapor, carried by the gas, the latter is passed through a U-tube containing dry red phosphorus mixed with broken glass or beads:

$$2P + 3Br_2 \rightarrow 2PBr_3.$$
$$PBr_3 + 3H_2O \rightarrow 3HBr \uparrow + H_3PO_3.$$
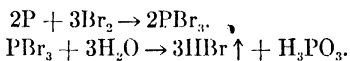
The bromine forms phosphorus tribromide, which is immediately decomposed by the water. The phosphorous acid H_3PO_3 re-
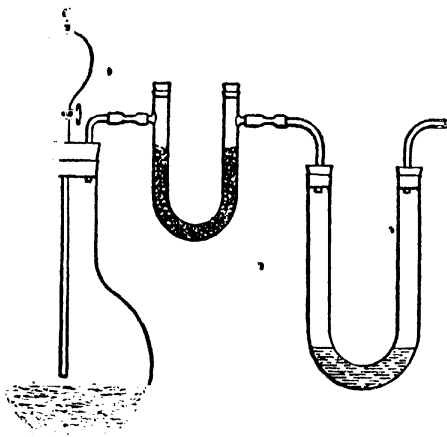
FIG. 79.

mains, dissolved in the water, in the flask. The second U-tube, containing water, may be attached when a solution of the gas is required. If it is omitted, the gas can be collected in a jar by upward displacement of air.

It might seem that a simpler action would be that of sulphuric acid upon a bromide (compare p. 162):

$$H_2SO_4 + KBr \rightarrow KHSO_4 + HBr \uparrow.$$
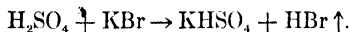
This action does take place, but the hydrogen bromide formed, being less stable than HCl, is oxidized rapidly by the concentrated sulphuric acid, so that, although some of the gas escapes

oxidation, it is mixed with much free bromine and sulphur dioxide: $H_2SO_4 + 2HBr \rightarrow SO_2 + 2H_2O + Br_2$. This action, indeed, enables us to *recognize* a bromide, by the color of the bromine vapor and the fuming of the hydrogen bromide produced.

Hydrolysis. — The interaction of water with phosphorus tribromide (foregoing section) illustrates an important property of water (p. 82). The action is **a double decomposition in which water is o.. of the interacting substances** and is called **an hydrolysis** (Greek, *loosening by water*). The water divides into the radicals H and OH, and the former unites with the more active non-metal in the substance (the bromine, in PBr_3) and the hydroxyl with the other element. For example,

$$P \begin{array}{ccc} Cl & H & -OH \\ Cl & + & H \end{array} \begin{array}{c} -OH \\ -OH \end{array} \rightarrow 3HCl + P \begin{array}{c} OH \\ OH \\ OH \end{array}$$
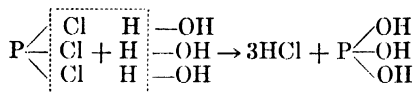
All the halides of the non-metals are thus hydrolyzed, as are also some other classes of compounds.

Note that the halogen compounds of phosphorus are essentially different in their general properties from the halogen compounds of the metals. They are *not salts*.

Physical Properties of Hydrogen Bromide. — Hydrogen bromide is a colorless gas with a sharp odor. It is two and a half times as heavy as air. It is easily reduced to the liquid condition (b.-p. $-69°$). It is exceedingly soluble in water, and in contact with moist air condenses the water vapor to clouds of liquid particles. Pure hydrogen bromide, whether in the gaseous condition or in the liquefied form, is a nonconductor of electricity.

Chemical Properties of Hydrogen Bromide. — Its chemical properties are like those of hydrogen chloride (p. 166). It is somewhat less stable, and dissociation begins to be noticeable at 800°. When free from water, it is not an acid (see below). The gas interacts vigorously with chlorine, hydrogen chloride and free bromine being produced, $2HBr + Cl_2 \rightarrow 2HCl + Br_2$. What are the relative volumes (p. 189)?

Chemical Properties of Hydrobromic Acid. — The solution of hydrogen bromide in water is an active acid (see p. 61). It conducts electricity extremely well. In contact with certain metals, and with oxides of metals and hydroxides of metals, it behaves exactly like hydrochloric acid (p. 167). In the first case, hydrogen is set free and the bromide of the metal produced. In the other two cases, water and the bromides of the metals are produced. For example: $Zn(OH)_2 + 2HBr \rightarrow ZnBr_2 + 2H_2O$. As an *acid*, hydrobromic acid gives double decomposition with bases and salts. Thus, with a salt of silver, we get a cream-colored precipitate of insoluble silver bromide:

$$AgNO_3 + HBr \rightarrow AgBr \downarrow + HNO_3.$$
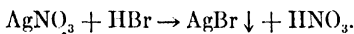
Chlorine-water, added to a solution of any bromide, displaces the bromine, which may be recognized by its brown color (test for a bromide):

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2.$$
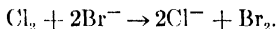
A few drops of carbon disulphide, shaken with the mixture, will settle to the bottom, carrying the brown bromine with it in a more concentrated, easily recognizable form (compare p. 158).

Oxidizing agents, such as manganese dioxide MnO_2, also liberate bromine from hydrobromic acid (compare p. 178).

Uses of Compounds of Bromine. — Bromine is manufactured in large amounts in Germany and in the United States. It is employed to make potassium bromide and other bromides. These are utilized in medicine, and to precipitate silver bromide in the manufacture of photographic films and plates.

IODINE I₂

Sources. — Iodine was formerly all obtained from seaweed (kelp), certain species of which use the traces of organic compounds of iodine in sea water as part of their food. The dried seaweed is carbonized in retorts, and sodium iodide remains in the residue, along with much sodium carbonate and carbon. In an improved process the iodine compounds are dissolved out of the

kelp, and from the latter a sort of gelatin, named **algin,** is extracted.

The greater part of our supply of iodine is at present obtained from sodium iodate $NaIO_3$, which forms about 0.2 per cent of crude Chile saltpeter (see p. 388).

Preparation. — The processes for obtaining iodine from an iodide are precisely the same as those for bromine from a bromide. In France chlorine is used to displace the iodine:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2 \downarrow.$$
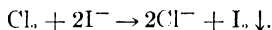
The precipitate of iodine is pressed free from the solution.

In Great Britain the iodide is mixed with manganese dioxide and sulphuric acid and heated:

$$3H_2SO_4 + MnO_2 + 2NaI \rightarrow MnSO_4 + 2NaHSO_4 + 2H_2O + I_2 \uparrow.$$

Iodine vapor condenses upon a cold surface, not to the liquid, but directly to the solid, crystalline form. Distillation which gives a solid product is called **sublimation.** The crude iodine is purified by repetition of this process.

Physical Properties. — Iodine (Gk., *like a violet*) is a black, solid substance (sp. gr. 5), exhibiting large crystalline plates of rhombic form. It melts at 114°, and boils at 184°. The vapor has at first a reddish-violet tint, and on being more strongly heated becomes deep blue (see next section).

Iodine is very slightly soluble in water (about 1 : 6000), and the solution has a scarcely perceptible brown tint. It is much more soluble in carbon disulphide (p. 16) and in chloroform, in which it gives violet solutions. In alcohol it gives a solution which is brown, the iodine being in a condition of feeble combination, and not simply in solution. An aqueous solution of potassium iodide, hydrogen iodide, or any other iodide, has likewise the power to take up large quantities of iodine. Here the formation of definite compounds (such as, $KI + I_2 \rightleftarrows KI_3$), by a reversible action, accounts for the amount of iodine taken up.

The behavior of free iodine towards starch forms a distinctive *test* for both substances (see p. 5). The pale-brown aqueous solution, for example, when added to starch emulsion, produces a

deep-blue color. This blue substance is not a chemical compound. The iodine is adsorbed by the starch, which is in colloidal suspension (see p. 138).

Chemical Properties. — The molecular weight of iodine, ascertained by weighing the vapor at temperatures from the boiling-point up to 700°, is 253.8. The atomic weight being 126.92, the molecule contains two atoms. Beyond 700°, the vapor diminishes in density more rapidly than Charles' law would lead us to expect, and at 1700° the molecular weight has fallen to 127 (see p. 122). As the vapor is heated, a larger and larger proportion of the molecules is broken up, until the decomposition has become complete. As in all cases of dissociation, when the vapor is cooled the atoms recombine to form molecules. This is the most notable case in which we encounter both the monatomic and the diatomic forms of the same element. The heat given out when the atoms reunite to form the molecules is very considerable $(2I \rightleftarrows I_2 + 28,500$ cal.), indicating that the chemical union of two atoms of identical nature may be as vigorous as that of two atoms of different chemical substances. The heat of union of atomic hydrogen (p. 118) is even greater $(2H \rightleftarrows H_2 + 90,000$ cal.). In both cases, in accordance with Van't Hoff's law (p. 216), raising the temperature increases the dissociation, because that is the direction in which heat is absorbed.

Iodine *unites* very slowly with hydrogen, even when heated. It unites directly with some non-metals and with the majority of the metals. When phosphorus is presented in the white form (see p. 404), the action takes place spontaneously without the assistance of heat. Both chlorine and bromine *displace* iodine from combination with hydrogen and the metals $(2HI + Br_2 \rightarrow 2HBr + I_2)$.

The Direct Union of Hydrogen and Iodine. — The slow union of hydrogen and iodine referred to above, giving hydrogen iodide, is a reversible reaction:

$$2HI \rightleftarrows H_2 + I_2.$$
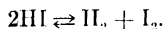
That is to say, whether we charge a tube with hydrogen iodide, or with an equal amount of the elements in the correct propor-

tions by weight, if we place both tubes in a bath, and keep them thus at the same temperature, the contents of the tubes will after a time be identical (p. 204).

At 283°, a mixture of hydrogen and iodine yields 82 per cent of hydrogen iodide and 18 per cent of the uncombined elements. At 445°, the yield of hydrogen iodide is 79 per cent, and at 508° only 76 per cent. Since the elements increase in quantity as the temperature rises, we infer (see p. 216) that the dissociation of the compound *absorbs heat.* At 400°, the value is:

$$2HI + 535 \text{ cal.} \leftrightarrows H_2 + I_2.$$
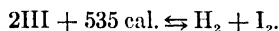
Curiously enough, at low temperatures, the action is *exothermal.* Thus at 18°:

$$2HI \leftrightarrows H_2 + I_2 + 6100 \text{ cal.}$$
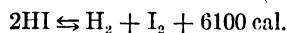
A reversal of the sign of the heat of a reaction is not uncommon. Thus, ammonia and hydrogen bromide, up to about 320°, give out heat in combining. Beyond that temperature, ammonium bromide gives out heat in dissociating (A. Smith); and so above 320° the degree of dissociation into NH_3 and HBr in the saturated vapor is less the higher the temperature.

Hydrogen Iodide HI, Preparation. — The gas is most conveniently prepared by a process similar to that employed in the case of hydrogen bromide (Fig. 79, p. 273). Red phosphorus and iodine are mixed, and water is allowed to fall drop by drop upon the mass:

$$2P + 3I_2 \rightarrow 2PI_3.$$
$$PI_3 + 3H_2O \rightarrow 3HI + H_3PO_3.$$
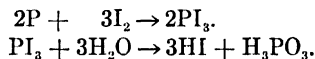
The action of sulphuric acid upon an iodide does **not** give pure hydrogen iodide, although the action $NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$ does take place (compare p. 273). Hydrogen iodide, being much less stable than even hydrogen bromide, is a more active reducing agent, and reduces the sulphuric acid to hydrogen sulphide. The odor of this gas is therefore very conspicuous when an iodide is moistened with sulphuric acid:

$$H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2.$$

The violet vapor of iodine becomes visible if the test-tube is warmed. A rough *test* for an iodide is afforded by this action.

Another method of making hydrogen iodide is frequently employed when a solution of the gas in water is required, and not the gas itself. Powdered iodine is suspended in water, and hydrogen sulphide gas is introduced through a tube in a continuous stream. The iodine dissolves slowly in the water and acts by displacement upon the sulphide ion $S^=$, derived from the solution of H_2S in water. Sulphur separates in a fine powder, and a solution of hydrogen iodide (hydriodic acid) is formed in accordance with the equation:

$$2H^+ + S^= + I_2 \rightarrow 2H^+ + 2I^- + S \downarrow.$$
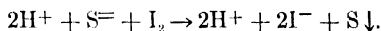
The solution is freed from the deposit of sulphur by filtration, and may be concentrated to 57 per cent of hydriodic acid by distilling off the water.

Physical Properties of Hydrogen Iodide. — Hydrogen iodide is a colorless gas with a sharp odor. Its molecular weight is 128 and it is therefore much heavier than air, the average weight of whose molecules is 28.95 (p. 134). It is a nonconductor of electricity, both in the gaseous and in the liquefied conditions. It is exceedingly soluble in water, so that at 10° 30 grams of water will absorb 70 grams of the gas. The behavior of this solution is similar to that of hydrogen chloride and hydrogen bromide (see p. 166). The mixture of constant boiling-point distils over at 127° (at 760 mm.), and contains 57 per cent of hydrogen iodide.

Chemical Properties of Hydrogen Iodide. — Hydrogen iodide is the least stable of the hydrogen halides. When heated it begins visibly to decompose into its constituents at 180°. On account of the ease with which it parts with the hydrogen which it contains, it can be burned in oxygen gas, $4HI + O_2 \rightarrow 2H_2O + 2I_2$. When the gas is mixed with chlorine, a violent chemical change, accompanied by a flash of light, occurs, the iodine is set free, and hydrogen chloride is produced, $Cl_2 + 2HI \rightarrow 2HCl + I_2$. Bromine vapor will similarly displace the iodine from hydrogen iodide.

Chemical Properties of Hydriodic Acid. — In most respects the aqueous solution behaves exactly like hydrochloric and hydrobromic acids. With oxidizing agents, for example, such as manganese dioxide, it readily gives free iodine, just as the others (p. 178) give free chlorine and bromine, respectively. Here, however, the oxidation is so much more easily carried out, that it is slowly effected by atmospheric oxygen, so that hydriodic acid left exposed to the air gradually becomes brown $(O_2 + 4HI \rightarrow 2H_2O + 2I_2)$.

The iodide-ion I^-, which hydriodic acid contains, gives, with any soluble salt of silver, a precipitate of insoluble yellow silver iodide AgI:

$$AgNO_3 + HI \rightarrow AgI \downarrow + HNO_3.$$
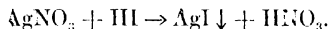
Chlorine-water or bromine-water, added to a solution of hydriodic acid or any other iodide, displaces the iodine:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2.$$

The free iodine, even if present in minute amounts, may be *recognized* by shaking the liquid with a few drops of carbon disulphide. The iodine gives a violet solution in the latter. A still more delicate *test* is the addition of a drop of very thin starch paste, which gives a deep-blue tint with *free* iodine (see p. 276). Filter paper dipped in starch paste and dried can also be used, by touching it with a drop of the solution containing the free iodine.

Uses of Iodine and Its Compounds. — The alcoholic solution (tincture of iodine), painted over the skin, reduces swellings and inflammation. **Iodoform** CHI_3 is a solid used for similar purposes. **Iodothyrin** is an organic compound found in the human thyroid gland, as well as that of other animals. An extract of sheeps' thyroids (thyroxin) is administered with remarkable success in cases of degeneration caused by abnormally small natural development of this gland (cretinism). Potassium iodide is also used in medicine, to cause absorption of blood-clots and effusions of blood, for example in the eye. Silver iodide is contained in the coating on photographic plates and films.

FLUORINE F_2.

The discussion of this element should logically have preceded that of chlorine, since it is, of all the members of the halogen family, the most active. Chlorine was taken up first, however, because its compounds are more familiar. Fluorine is found in nature chiefly in the mineral **fluorite,** calcium fluoride CaF_2, and in **cryolite,** a double fluoride of aluminium and sodium $3NaF,AlF_3$.

Fig. 80.

Preparation. — When a solution of hydrofluoric acid is heated with manganese dioxide, oxidation does not occur and free fluorine is not produced. Until recently all efforts to isolate the element failed. It was perfectly understood that the reason of these failures lay in the greater chemical activity of fluorine, which made it more difficult of separation from any state of combination than the other halogens. Its preparation was finally achieved by Moissan (1886) by the decomposition of anhydrous hydrogen fluoride, which is liquid below 19°, by means of electricity. The apparatus (Fig. 80) is made of copper, which, after receiving a thin coating of the fluoride, is not further affected. To reduce the tendency to chemical union, the whole is immersed in a bath giving a temperature between $-23°$ and $-40°$. The electrodes are made of an alloy of platinum and iridium, which is the only material that can resist the action of the fluorine. Hydrogen fluoride, like other hydrogen halides, is a nonconductor of electricity, and a small quantity of potassium-hydrogen fluoride KHF_2 has to be added to enable the current of electricity to pass. The fluorine is set free at the positive electrode, and hydrogen appears at the negative. The U-tube is closed, after the introduction of the hydrogen fluoride, by means of blocks made of calcium fluoride, which is naturally unable further to enter into combination with fluorine. For the reception and examination of
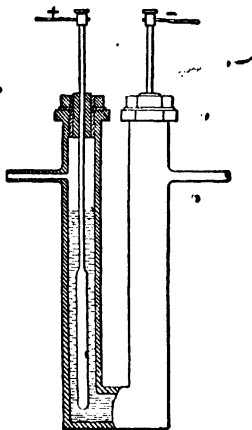
the fluorine gas, other copper tubes can be screwed on to the side neck of the apparatus, and, when necessary, small windows of calcium fluoride can be provided.

Physical Properties. — Fluorine is a gas whose color is like that of chlorine, but somewhat paler. Its density (38) shows that the molecule is diatomic (F_2). The gas is the most difficult of the halogens to liquefy. The liquid boils at $-186°$.

Chemical Properties. — Fluorine unites with every element, with the exception of oxygen, chlorine, nitrogen, and the members of the helium family, and in many cases does so with such vigor that the union begins spontaneously without the assistance of external heat. Dry platinum and gold are the elements least affected. It explodes with hydrogen at the ordinary temperature, without the assistance of sunlight. On the introduction of a drop of water into a tube of fluorine, the oxygen of the water (vapor) is instantly *displaced* by fluorine, and the vessel is filled with the deep-blue gas, ozone (see p. 286): $3F_2 + 3H_2O \rightarrow 3H_2F_2 + O_3$.

Fluorine displaces the chlorine in hydrogen chloride as easily as chlorine in turn displaces bromine or iodine.

Hydrogen Fluoride H_2F_2, Preparation. — Pure, dry hydrogen fluoride is best made by heating potassium-hydrogen fluoride, $2KHF_2 \rightleftarrows K_2F_2 + H_2F_2 \uparrow$. For ordinary purposes, however, the preparation of an aqueous solution is the ultimate object. Usually powdered calcium fluoride is treated with concentrated sulphuric acid, and the mixture distilled in a retort of platinum or lead:

$$CaF_2 + H_2SO_4 \rightleftarrows CaSO_4 + H_2F_2 \uparrow.$$
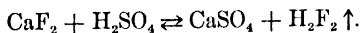
The hydrogen fluoride passes over and is caught in distilled water. The aqueous solution of hydrofluoric acid thus obtained has to be kept in vessels made of lead, rubber, or paraffin, as glass interacts with the acid with great rapidity (see below).

Physical Properties of Hydrogen Fluoride. — The vapor of hydrogen fluoride can be condensed to a colorless *liquid* boiling at 19.4°. Being very *soluble in water,* it fumes strongly in moist air. The vapor *density* below 40° corresponds with the formula

H_2F_2, but at higher temperatures gradual dissociation to HF occurs.

Properties of Hydrofluoric Acid. — The aqueous solution of hydrogen fluoride has all the properties of a *transition acid* (see p. 244). Metals like zinc and magnesium interact with hydrofluoric acid with evolution of hydrogen (p. 64). The action is less violent than with other halogen acids. The acid interacts with oxides and hydroxides, forming fluorides (p. 167). One of the commonest salts of hydrofluoric acid is potassium-hydrogen fluoride, or the acid fluoride of potassium KHF_2, mentioned above.

Hydrofluoric acid has, in addition, the remarkable property of acting upon *silica* SiO_2 (sand), and silicates, to give **silicon tetrafluoride** SiF_4 (a gas). Hence it attacks glass, which is essentially a mixture of sodium silicate Na_2SiO_3 and calcium silicate $CaSiO_3$:

$$SiO_2 + 2H_2F_2 \rightarrow SiF_4 + 2H_2O.$$
$$CaSiO_3 + 3H_2F_2 \rightarrow SiF_4 + CaF_2 + 3H_2O.$$
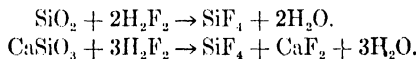
Thus, when glass is covered with melted paraffin to protect the surface, and marks or letters are made by removing the paraffin with a sharp instrument, hydrogen fluoride will decompose the glass at the parts thus exposed (*test* for fluorine). In this way the graduation on thermometer stems and lettering on glass are frequently made. The vapor gives rough, easily visible depressions, the solution smooth, glossy ones.

On account of this property, hydrofluoric acid is used for removing adhering sand from castings and for cleaning the outside of granite and sandstone buildings.

THE HALOGENS AS A FAMILY

The reader is recommended to compare carefully the properties of the several halogens and their compounds with hydrogen. It will be found that, while very striking similarities exist throughout the whole halogen family in the case of nearly every physical and chemical property, there is always a regular gradation in properties in the order of the atomic weights,

namely F, Cl, Br, I. A few examples are noted below; the student should tabulate the rest himself for his own convenience.

Color in liquid state: F_2 yellow; Cl_2 greenish-yellow; Br_2 brown; I_2 deep violet.

Boiling-point: $F_2 - 187°$; $Cl_2 -34°$; Br_2 59°; I_2 184°.

Action on hydrogen: F_2 very rapid action in cold, without light; Cl_2 action rapid in cold, only with strong light; Br_2 action rapid only when heated; I_2 action slow and incomplete even when heated.

As an aid to the memory, such a table is exceedingly valuable. But it is really not necessary to attempt to memorize *all the properties* of each halogen and of each halogen compound *separately.* The properties of bromine, for example, are all intermediate between those of chlorine and iodine. Indeed, when bromine was first examined by Liebig, he thought it was an unstable compound of chlorine and iodine, and so missed gaining the credit of its discovery as an element.

The *activity* of the halogens, as is evident from their action on hydrogen, decreases in the order of increasing atomic weight. This is seen also in their displacement reactions in solutions. Thus we have found that chlorine displaces bromine from bromides and that bromine displaces iodine from iodides. Fluorine is able to displace even chlorine from chlorides: $2Cl^- + F_2 \rightarrow 2F^- + Cl_2$. When we note also that the halogens displace sulphur from sulphides (compare p. 279) and that oxygen displaces iodine from hydriodic acid, we are able to draw up an *order* of *activity* for the non-metals, similar to the activity order for the metals. This order of activity expresses the order of preference of the non-metals for assuming the ionic state, or for gaining electrons (see p. 267). Starting from the top, it is F, Cl, Br, O, I, S.

A last point worthy of mention is that some of the properties of fluorides are peculiar. Thus hydrogen fluoride at low temperatures has the formula H_2F_2, and its solution in water is not highly ionized. We shall see later that it is usual for the first member of a family of elements or compounds to exhibit a few peculiarities. In fact we have already noted, at the beginning of

this chapter, one peculiarity of the first of all the elements, hydrogen. Although a non-metal, it gives a *positive* ion H^+.

Exercises. — 1. Tabulate the properties of fluorine, chlorine, bromine and iodine, and of their compounds with hydrogen.

2. How should you distinguish by chemical reactions the chloride, bromide, iodide, and fluoride, (a) of hydrogen, (b) of sodium from one another?

3. Write equations for the action, (a) of chlorine upon a solution of hydrogen sulphide, (b) of bromine upon a solution of hydrogen iodide, (c) of oxygen upon a solution of hydrogen iodide, (d) of fluorine upon a solution of hydrogen iodide.

4. Why does hydriodic acid, when left in the air, become brown in color?

5. Make a list of all the acids we have encountered, and note which are weak and which strong.

6. How should you make potassium bromide, starting with, (a) potassium and bromine, (b) hydrogen bromide, (c) potassium iodide?

7. Rewrite the equation for the action of hydrobromic acid on silver nitrate solution in full ionic form.

8. At a given temperature, would increasing the pressure in a mixture of hydrogen and bromine vapor render the union more or less complete? Is the action more complete at a high or at a low temperature?

CHAPTER XX

OXIDIZING SUBSTANCES

In the preceding chapters we have encountered several rather
· ·confusing *oxidizing reactions*. For example, in the preparation
of chlorine by the action of KMnO$_4$ on HCl (p. 177), it was stated
that the hydrogen chloride was oxidized to chlorine and the potas-
sium permanganate reduced to manganous chloride. The student
may have found it difficult to understand how we can regard
a substance as oxidized when no oxygen is added to it. In order
to explain oxidations more clearly, particularly in connection with
the conception of valence, we must now learn more about oxida-
tion in general. We can do this best through the study of three
oxidizing substances which are of a simpler nature and are all
in common use. These are **ozone, hydrogen peroxide,** and **hypo-
chlorous acid.**

OZONE O$_3$

A fresh, penetrating odor, resembling that of very dilute
,chlorine, was noticed by van Marum (1785) near an electrical
machine in operation. Schönbein (1840) showed that the odor
was that of a distinct substance, which he named ozone (Greek,
to smell), and he discovered a number of ways of obtaining it.
It is very questionable whether there is any ozone in the air, ex-
cepting temporarily in the immediate neighborhood of a natural
or artificial discharge of electricity.

Preparation of Ozone O$_3$.—The most satisfactory way of pre-
paring ozone is to pass a silent electrical discharge through oxy-
gen. The apparatus (Fig. 81) consists of two co-axial glass tubes,
between which the oxygen flows. The discharge is produced by
connecting an outer layer of tinfoil on the outer tube, and an inner
layer of tinfoil in the inner tube with the poles of an induction

coil. With dry, cold oxygen, about 7.5 per cent of the gas is
turned into ozone.

, Traces of ozone are found in the oxygen generated by elec-
trolysis of dilute sulphuric acid (p. 66). It arises during the
slow oxidation of phosphorus by the air, resulting, probably,
from the decomposition of unstable, highly oxidized bodies which
are formed during the action. Oxygen containing 15 per cent of
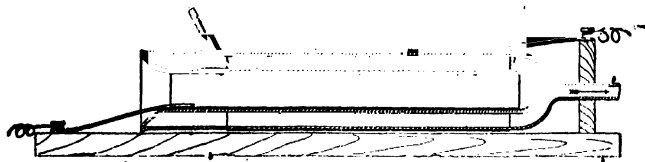
FIG. 81.

it is produced by the interaction of fluorine and water (p. 282).
Ozone is formed also when a jet of burning hydrogen, or an elec-
trically heated loop of platinum wire, is immersed in liquid
oxygen. This method shows that ozone is formed at high tem-
peratures, and survives when cooled suddenly by the liquid
oxygen.

Physical Properties of Ozone. — Ozone is a gas of blue color.
It boils at $-119°$, so that when a mixture of oxygen and ozone is
led through a U-tube immersed in liquid oxygen ($-182.5°$), the
ozone collects in the tube as a deep-blue fluid. Ozone is much
more soluble in water than is oxygen. At $12°$, 100 volumes of
water would dissolve 50 volumes of the gas at one atmosphere
pressure.

Chemical Properties of Ozone. — The density of ozone is one-
half greater than that of oxygen. Its molecular weight is there-
fore 48, and its formula O_3. Being formed with absorption of
energy, ozone is most stable at very high temperatures (Van't
Hoff's law, p. 216). •

$$3O_2 + 61,400 \text{ cal.} \rightleftarrows 2O_3.$$

When produced in cold oxygen, by energy from electric waves, it
decomposes slowly. The attainment of equilibrium in this case,

like all others, is hastened by raising the temperature. Equilibrium, with almost no ozone, is reached practically instantly at 250–300°. Liquid ozone sometimes decomposes explosively. As the equation shows, three volumes of oxygen give two of ozone.

Ozone is a much more active oxidizing agent than oxygen. Mercury and silver, which are not affected by the latter, are converted into oxides by the former. Silver gives the peroxide, Ag_2O_2, thus:

$$2Ag + 2O_3 \rightarrow Ag_2O_2 + 2O_2.$$
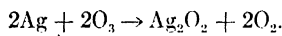
Paper dipped in starch emulsion containing a little potassium iodide is used as a **test** for ozone:

$$O_3 + 2KI + H_2O \rightarrow O_2 + 2KOH + I_2.$$
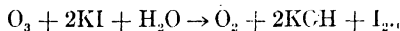
The iodine gives a deep-blue color to the starch (see p. 276). This test, however, will not distinguish ozone from chlorine or hydrogen peroxide, and may, therefore, be used only in the absence of these substances.

Ozone also removes the color from many of the vegetable coloring matters and artificial dyes. It should be understood that the great majority of the complex compounds of carbon are colorless. Even a slight chemical change, affecting only one or two of the atoms in a complex molecule, is thus almost sure to give a colorless or much less strongly colored material. Indigo, $C_{16}H_{10}N_2O_2$, which has a deep-blue color, is an example of a vegetable dye that is also made artificially. When ozonized air is bubbled through a dilute solution of this dye (as indigo-carmine), the indigo is oxidized to isatin $C_8H_5NO_2$, and the color disappears (see below).

Ozone is used commercially in bleaching oils, waxes, ivory, flour, and starch. It is employed also for sterilizing drinking water in Petrograd, Lille, and other cities. For this purpose, however, bleaching powder is less expensive.

Oxidizing Agents, and Explanation of their Activity. — When ozone turns into oxygen much heat is liberated (equation, above). Ozone possesses, therefore, much more internal energy than does oxygen. On this account it brings to the task of oxi-

dizing any substance more energy than does oxygen itself, and is therefore more efficient. Thus, free oxygen does not interact in the cold with indigo, or with silver or potassium iodide (see above), while ozone oxidizes them rapidly.

The reason for this difference is shown more clearly by means of thermochemical equations (p. 202). When one gram-molecular weight of indigo is oxidized by ozone to isatin, 63,200 calories of heat are liberated:

• $C_{16}H_{10}N_2O_2 + 2O_3 \rightarrow 2C_8H_5NO_2 + 2O_2 + 63,200$ calories. (1)
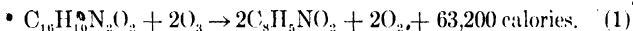
But we have seen above that the same quantity of ozone, decomposing into oxygen, liberates 61,400 calories of heat:- -

$$2O_3 \rightarrow 3O_2 + 61,400 \text{ calories.} \qquad \cdot(2)$$
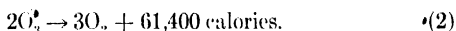
Now it is a characteristic of thermochemical reactions that, when they are added or subtracted, the heat effect of the resultant reaction is equal to the sum or difference of the original reactions. This is, indeed, a necessary consequence of the law of conservation of energy (p. 197). Thus, whether we burn carbon (p. 419) directly to carbon dioxide CO_2, or whether we burn it first to carbon monoxide CO and then burn this to CO_2, exactly the same amount of heat is evolved:

$$
\begin{array}{l}
2C + O_2 \rightarrow 2CO + 58,000 \text{ calories} \\
\underline{2CO + O_2 \rightarrow 2CO_2 + 135,800 \text{ calories}} \\
2C + 2O_2 \rightarrow 2CO_2 + 193,800 \text{ calories}
\end{array}
$$
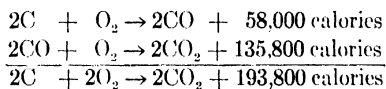
Employing this principle, we can discover what would be the amount of heat liberated if indigo could be oxidized to isatin by oxygen gas, by subtracting equation (2) from equation (1) above, even although the reaction so represented cannot be conveniently carried out. The result is:

$$C_{16}H_{10}N_2O_2 + O_2 \rightarrow 2C_8H_5NO_2 + 1,800 \text{ calories.} \qquad (3)$$
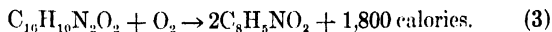
The heat liberated in equation (1) is consequently 35 times as great as in equation (3). In view of what has been said in a previous chapter (p. 201) regarding the speed of a chemical change, and the quantity of energy available because of it, the

greater efficiency of ozone as an oxidizing agent will now be readily understood.

It should be noted that when ozone acts as an oxidizing agent, usually only one of the atoms, of oxygen in each molecule plays this part, and oxygen gas is formed. This is illustrated in all the three examples cited in the preceding section.

Allotropic Modifications. — We have seen that a substance may exist in more than the three regular states, solid, liquid, and gaseous. When a simple substance shows more than one form, in the same state, like oxygen and ozone, we call them **allotropic modifications.**

HYDROGEN PEROXIDE H_2O_2

Hydrogen peroxide is found in minute amounts in rain and snow. It is formed in small quantities, in a way not at present fully understood, when moist metals, like zinc, lead, and copper rust.

Preparation. — Sodium peroxide Na_2O_2, produced by burning sodium in dry air, can be dissolved, a little at a time, in *ice-cold* water. When this solution is acidified with hydrochloric or sulphuric acid, a double decomposition takes place:

$$Na_2O_2 + 2HCl \rightarrow 2NaCl + H_2O_2$$
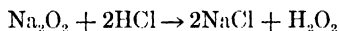
and a dilute solution of hydrogen peroxide (mixed with common salt) is obtained. The nature of the action shows the product to be an acid, with the negative radical $O_2{}''$.

For manufacturing purposes it is more convenient to use barium peroxide BaO_2, suspended in water, and sulphuric acid:

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + H_2O_2$$
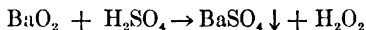
because the precipitation of insoluble barium sulphate carries the reaction to completion. The precipitate is filtered off and a clear solution of hydrogen peroxide obtained.

Phosphoric acid is largely employed instead of sulphuric acid in the commercial manufacture of hydrogen peroxide, and great care is taken to precipitate the other products and all impurities from the solution.

An aqueous solution is also obtained by passing carbon dioxide through barium peroxide suspended in water:

$$BaO_2 + CO_2 + H_2O \leftrightarrows BaCO_3 \downarrow + H_2O_2.$$
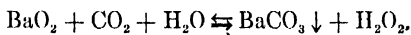
Pure hydrogen peroxide is isolated from any of these solutions by distillation under reduced pressure. To secure the low pressure, the ordinary distilling apparatus (Fig. 41, p. 82) is made completely air-tight, and is connected by a branch tube with a water-pump. Hydrogen peroxide is much less volatile than water, but decomposes into water and oxygen violently at 100°. Hence the lower pressure is required to make possible its volatilization at a temperature below this point. At 26 mm. pressure, the water begins to pass off first (at about 27°). The last portion of the liquid boils at 69° and is hydrogen peroxide.

By evaporating the commercial (3 per cent) solution at 70°, a liquid containing 45 per cent of hydrogen peroxide may be made without much loss of the material by volatilization.

Physical Properties. — Hydrogen peroxide (100%) is a syrupy liquid of sp. gr. 1.5. It blisters the skin and, when diluted, has a disagreeable metallic taste. The pure substance freezes at − 1°.

Chemical Properties. — Hydrogen peroxide (100%) is very **unstable,** and decomposes slowly even at low temperatures. The dilute aqueous solution, when free from impurities, keeps fairly well. The presence of a trace of free acid or of certain organic substances, such as acetanilide, increases its stability. Free alkalies and most salts assist the decomposition; hence the necessity for purifying the commercial solution. Addition of powdered metals, of manganese dioxide, or of charcoal (*contact action*) causes effervescence even in dilute solutions, and oxygen escapes:

$$2H_2O_2 \rightarrow 2H_2O + O_2.$$
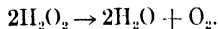
Since the substance cannot be vaporized, even at low pressure, without some decomposition, its molecular weight has been determined by the freezing-point method. It has been found that a solution containing 31.8 g. of the substance in 1000 g. of water

freezes at − 1.86°. Hence, by reference to p. 155, we obtain **31.8** as the molecular weight (approximate only, see immediately below). Now the formula HO corresponds to a molecular weight of **17** and H_2O_2 to one of **34.** It is evident, therefore, that the latter is the correct formula.

Hydrogen peroxide, in solution in water, is a **feeble acid.** The fact that it is slightly ionized in aqueous solution helps to explain the slightly abnormal freezing-point depression value found in the preceding paragraph (see p. 245). As an acid it enters into double decomposition readily, and the peroxides are salts with the negative radical O_2^{II}. Thus, when hydrogen peroxide is added to solutions of barium and strontium hydroxides, the hydrated peroxides appear as crystalline precipitates:

$$Sr(OH)_2 + H_2O_2 \rightleftarrows 2H_2O + SrO_2.$$
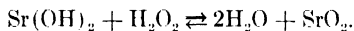
The precipitation involves another equilibrium: $SrO_2 + 8H_2O \rightleftarrows SrO_2,8H_2O$ (solid).

The bivalent character of the radical O_2, alluded to above, may be more clearly expressed by the following graphic formulæ for hydrogen peroxide and its most familiar salt, barium peroxide:

$$H - O - O - H \qquad\qquad Ba{\underset{O}{\overset{O}{\diagdown\;\big|}}}$$

' The formation of a beautiful blue substance by the action of hydrogen peroxide upon dichromic acid is used as a **test.** The test is carried out by adding a drop of potassium dichromate to an *acidulated* solution of the peroxide. The acid interacts with the dichromate, giving free dichromic acid:

$$H_2SO_4 + K_2Cr_2O_7 \rightleftarrows H_2Cr_2O_7 + K_2SO_4.$$
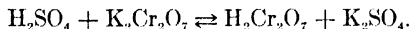
The blue substance, which is very unstable and quickly decomposes, is a perchromic acid. A blue, crystalline perchromic acid $(HO)_4Cr(OOH)_3$, which decomposes above − 30°, has been prepared. The blue substance has the property, unusual in inorganic compounds, of dissolving much more readily in ether than in water. It is also much less unstable when removed from the foreign materials in the aqueous solution. Hence the test is rendered more delicate by extracting the solution with a small

amount of ether. In the ethereal layer the color of the compound is more permanent, as well as more distinctly visible on account of the greater concentration.

Hydrogen peroxide is a much more active **oxidizing agent** than is free oxygen. This would be expected from the fact that it contains so much more internal energy than the water and oxygen into which it decomposes (p. 291), that 23,100 cal. are liberated in the decomposition of one gram-molecular weight. Thus, it liberates iodine from hydrogen iodide:

$$2HI + H_2O_2 \rightarrow 2H_2O + I_2.$$
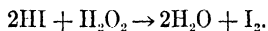
It converts sulphides into sulphates. The white lead (see p. 643) used in paintings is changed by the hydrogen sulphide in the air of cities to black lead sulphide: $Pb_3(OH)_2(CO_3)_2 + 3H_2S \rightarrow 3PbS + 4H_2O + 2CO_2$. This may be oxidized to white lead sulphate by means of hydrogen peroxide:

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O,$$
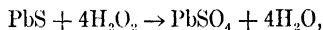
and in this way the original tints of the picture may be practically restored. Organic coloring matters are changed into colorless substances by an action similar to that of ozone (see p. 288). Hence hydrogen peroxide is used for bleaching silk, feathers, hair, and ivory, which would be destroyed by a more violent agent. The products of its decomposition, being water and oxygen only, are harmless, and, on this account, it is used in disinfecting (destroying organisms in) sores, and as a throat wash.

Hydrogen peroxide exercises the functions of a **reducing agent** in special cases, also. Thus, silver oxide is reduced by it to silver:

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2.$$
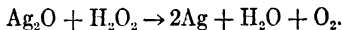
HYPOCHLOROUS ACID HOCl

Of the many compounds of the halogens which contain oxygen, *two* have already been mentioned—potassium chlorate $KClO_3$ (p. 30) and hypochlorous acid HOCl (p. 182). We shall here take up the latter of these as a third example of an oxidizing agent, and shall then devote the next chapter to a systematic discussion of the oxygen compounds of the halogens.

Pure Hypochlorous Acid. — A pure solution of the acid may be made by dissolving chlorine monoxide Cl_2O in water. **Chlorine monoxide** is a brownish-yellow, explosive gas, made by passing chlorine gas over warmed mercuric oxide:

$$2Cl_2 + HgO \rightarrow HgCl_2 + Cl_2O.$$
$$Cl_2O + H_2O \rightarrow 2HOCl.$$
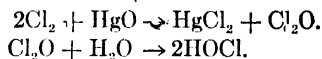
As *an acid,* hypochlorous acid is very weak, being very little decomposed into its ions, H^+ and $(OCl)^-$.

A concentrated solution tends to lose chlorine monoxide, the union with water being reversible. A second change which gradually takes place in a concentrated solution is a "self-oxidation" of part of the acid by another part to chloric acid $HClO_3$:

$$3HOCl \rightarrow HClO_3 + 2HCl.$$

It is *unstable in still another direction* even in dilute solution, exposure to sunlight being sufficient to cause it to give up oxygen, which rises in bubbles through the solution:

$$2HOCl \rightarrow 2HCl + O_2 \uparrow.$$
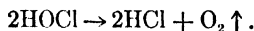
Heat is given out in the action, and the stable hydrochloric acid remains.

It is a most *active oxidizing agent,* because of this tendency to give up oxygen with liberation of energy. Thus, its solution oxidizes organic colored substances, producing colorless or less strongly colored ones:

$$C_{16}H_{10}N_2O_2 + 2HOCl \rightarrow 2C_8H_5NO_2 + 2HCl.$$
$$\text{indigo} \qquad\qquad\qquad \text{isatin}$$
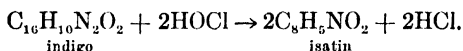
Used as a disinfectant (see p. 297), it oxidizes and destroys bacteria. Hypochlorous acid is *more energetic* as an oxidizing agent than is ozone or hydrogen peroxide, and is used extensively in *bleaching.*

Chlorine-Water. — It will be recalled that chlorine acts chemically upon water (p. 181):

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl$$
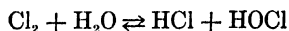
giving hydrochloric acid and hypochlorous acid. The action is reversible, and in half-saturated chlorine solution (freshly-made

and protected against bright sunlight, see p. 182) about one-third only of the chlorine has undergone the change shown in the equation. But, if a substance which can be oxidized, such as a dye (attached, perhaps, to cloth), is introduced into the solution, the HOCl which is present transfers its oxygen to the dye-stuff. This leaves HCl *alone* in the solution, and stops the backward reaction. Hence more of the chlorine acts upon the water, and more hypochlorous acid is formed. This, in turn, is used up. Thus, in a few moments, all the free chlorine is gone, only dilute hydrochloric acid remains, and a colorless organic compound is left on the cloth or in the solution.

Chlorine, itself is often, erroneously, spoken of as the bleaching agent. If a *dry*, colored cloth be hung for a week in chlorine, dried by having sulphuric acid in the bottle (Fig. 82), little or no change in color will occur. But a *wet* rag is bleached as soon as the chlorine has time to dissolve in the water and give the necessary hypochlorous acid.
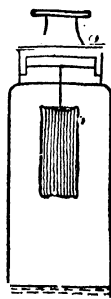
FIG. 82.

Preparation of Hypochlorites. — For industrial purposes, pure hypochlorites are not, as a rule, required. Hence, commercial **sodium** or **potassium hypochlorite** is prepared by the action of sodium or potassium hydroxide on chlorine-water. The latter contains both hydrochloric and hypochlorous acids, and so a solution containing a mixture of sodium or potassium chloride and hypochlorite is obtained:

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl. \qquad (1)$$
$$HCl + KOH \rightarrow KCl + H_2O. \qquad (2)$$
$$HOCl + KOH \rightarrow KOCl + H_2O. \qquad (3)$$
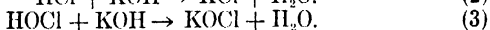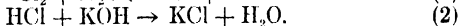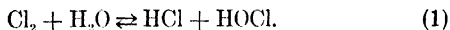
Although action (1) is only partial, being strongly reversible, the neutralization of the two acids in actions (2) and (3) displaces the first equilibrium, and all three actions proceed to completion. Omitting the water, which appears both among products and initial substances and in any case is present in large excess as a solvent, and omitting also the two acids, which are used up as quickly as they are produced by equation (1) and are not

amongst the actual products, we get, by addition of the three equations (compare p. 289), the final equation:

$$Cl_2 + 2KOH \rightarrow KCl + KOCl + H_2O.$$
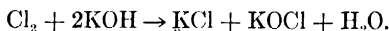
As lime is a less expensive alkali than is potassium or sodium hydroxide, it is largely used. The chlorine is led into chambers containing slaked lime $Ca(OH)_2$ spread on trays:

$$Ca(OH)_2 + Cl_2 \rightarrow Ca\begin{array}{c} Cl \\ \diagdown OCl \end{array} + H_2O.$$
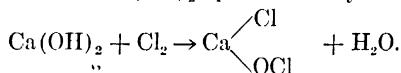
The product in this case is not a mixture, but a mixed salt (p. 247), known as **bleaching powder** or "chloride of lime." The action is not complete in practice, and the resultant product is always somewhat basic. It is only moderately soluble in water.

Hypochlorous Acid from Bleaching Powder. — 1. When bleaching powder is dissolved in water, being a salt, it is very extensively ionized (see formulation below). If now a concentrated solution of an *active* acid, that is, one giving a large concentration of hydrogen-ion, is added, the values of the products of the concentrations $[H^+] \times [Cl^-]$ and $[H^+] \times [OCl^-]$, on which depend the extent to which molecules of HCl and HOCl will be formed (p. 210), are large. HOCl, being little ionized, is formed extensively: HCl, being highly ionized, is formed in much smaller amount. Both, however, interact to produce chlorine and water, and this displaces the other equilibria. Hence an active acid decomposes the salt almost completely. A concentrated active acid gives, therefore, chlorine-water, and not pure hypochlorous acid.

$$CaCl(OCl) \rightleftarrows Ca^{++} + Cl^- + OCl^-$$
$$H_2SO_4 \rightleftarrows SO_4^= + H^+ + H^+$$
$$\Updownarrow \qquad \Updownarrow$$
$$HCl \qquad HOCl$$
$$\underbrace{\qquad\qquad\qquad}$$
$$\Updownarrow$$
$$H_2O + Cl_2$$
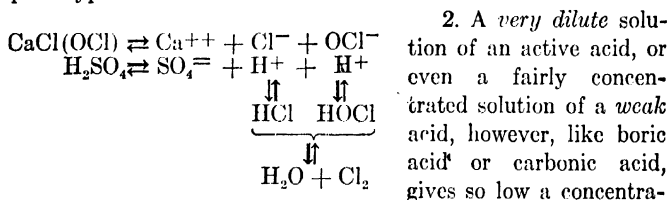
2. A *very dilute* solution of an active acid, or even a fairly concentrated solution of a *weak* acid, however, like boric acid or carbonic acid, gives so low a concentration of H^+ that union of this ion with OCl^- occurs to form the little ionized HOCl only, and practically no combination of H^+ with Cl^- takes place.

$$\left.\begin{array}{l} CaCl(OCl) \rightleftarrows Ca^{++} + Cl^- + OCl^- \\ H_2CO_3 \rightleftarrows CO_3^{=} + H^+ + H^+ \end{array}\right\} \rightleftarrows HOCl.$$
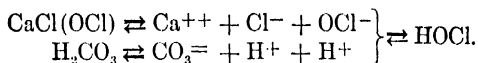
If now materials which it is desired to bleach by oxidation are introduced into the solution, the HOCl is used up, stopping the backward reaction and carrying the decomposition finally to completion.

Bleaching. — Cotton and linen, in their original states, are not pure white. Bleaching is therefore an extensive and most important industry. The yarn or cloth must first be freed from cotton-wax and tannin, since the former would hinder the action of the bleaching agent, and both would also make the subsequent dyeing uneven. The material is therefore first boiled with dilute caustic soda solution, and washed with water. The goods are then first "chemicked" in cold bleaching powder solution; next "soured" by immersion in *very dilute* sulphuric or hydrochloric acid; and finally washed with extreme thoroughness.

The final *washing*, to remove all traces of chlorine and bleaching powder, is absolutely necessary. If not removed, the hypochlorous acid acts gradually upon the cotton or linen, and "rots" it. Bleaching agents, when used in the household, carelessly, are liable to cause extensive damage from this cause. A dilute solution of sodium thiosulphate (photographers' "hypo," see p. 348) is often used, as "antichlor," to interact with and remove the last traces of chlorine.

Cotton and linen are composed of cellulose $(C_6H_{10}O_5)_y$, a rather inert substance, and one which is very slowly acted upon by dilute hypochlorous acid. Hence, with brief contact and proper handling, no damage is done. Wool, silk, and feathers, however, are composed largely of compounds (proteins) containing nitrogen (up to 15 per cent) in addition to the above three elements. Their constituent material interacts as easily with hypochlorous acid as do the traces of coloring substances. Hence, since the fabric itself would be attacked by this agent, sulphurous acid (p. 334) is used for bleaching these materials.

Bleaching Powder as a Disinfectant. — A disinfectant is a substance which destroys bacteria and other minute, and often

harmful, organisms. Bleaching powder CaCl(OCl) has a distinct odor. This is due to the slow action of the carbon dioxide and moisture of the air upon the salt, liberating hypochlorous acid. Bleaching powder, when scattered around, will therefore *disinfect* the surrounding air, because the hypochlorous acid thus liberated kills all bacteria present by *oxidation*.

When an epidemic of typhoid fever occurs, it is usually traced to the presence of colon bacilli and typhoid organisms in the *drinking water*. The most effective means of destroying these bacilli is to add, at the distributing point, a small proportion of bleaching powder (about 20 pounds per million gallons of water).

Recently, *chlorine-water* has in many cases taken the place of bleaching powder for this purpose. Cylinders of liquid chlorine (p. 180) were used in the Great War to kill germs as well as to kill Germans, all water supplies being sterilized, whenever possible, by the addition of very minute amounts of chlorine.

<div align="center">OXIDATION AND REDUCTION</div>

Oxidations Previously Mentioned. — The simplest oxidations are reactions in which free oxygen is actually used up, for example in the *union of oxygen* with metals and with non-metals:

$$2Cu + O_2 \rightarrow 2CuO.$$
$$S + O_2 \rightarrow SO_2.$$
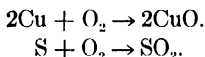
The displacement of another element from a compound by oxygen is also oxidation:

$$4HCl + O_2 \leftrightarrows 2H_2O + 2Cl_2.$$
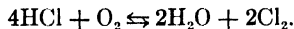
The transfer of combined oxygen from one substance to another in a reaction is again oxidation:

$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$
$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O.$$
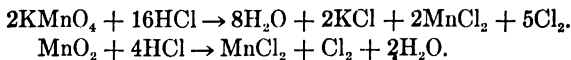
What is the substance oxidized in the last three reactions? It is *hydrochloric acid,* and the product of its oxidation is *chlorine.* True, we have added no oxygen to chlorine itself in any of these reactions, but we have done something which is exactly equivalent

to addition of oxygen, we have *taken away hydrogen*, and we have not replaced that hydrogen by any other positive element.

Note that *every oxidation is accompanied by reduction of the oxidizing agent.* Thus in the first of the three reactions just discussed, the free oxygen is reduced to water. In the other reactions, $KMnO_4$ and MnO_2 are reduced to $MnCl_2$. In all three cases HCl is the *reducing agent.*

The appearance of a product that could be formed only by reduction is sometimes the first thing that calls our attention to the fact that an oxidizing action has occurred. When concentrated sulphuric acid acts upon hydrogen iodide (p. 278), the iodine vapor given off on warming shows that there was oxidation, but the *odor* of the hydrogen sulphide is the first thing we notice when doing the experiment:

$$H_2SO_4 + 8HI \rightarrow H_2S + 4H_2O + 4I_2.$$

Removal of the elements of water from a compound is *neither oxidation nor reduction,* for hydrogen and oxygen are *both* removed:

$$H_2CO_3 \rightarrow CO_2 + H_2O.$$
$$NH_4OH \rightarrow NH_3 + H_2O.$$
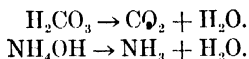
We can now see that oxidation, *in the above cases,* consists always in adding oxygen **or** removing hydrogen.

Other Cases of Oxidation. — But oxygen is only one of a class of elements which we call non-metallic or negative elements, so that we do not *restrict* the term "oxidation" to actions involving oxygen. Thus, forming a sulphide, by heating a metal with sulphur, is oxidation also:

$$Fe + S \rightarrow FeS.$$
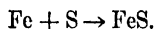
Similarly, changing ferrous chloride $FeCl_2$ to ferric chloride $FeCl_3$ is oxidation:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3.$$
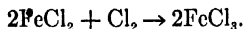
In every compound one of the elements is relatively positive and the other relatively negative. Iron is positive, sulphur and chlorine are negative.

Oxidation, then, is introducing, or increasing the proportion of the negative element, or removing, or reducing the proportion of the positive element. Reduction is the converse.

Oxidation and Valence. — Combining a metal with oxygen or sulphur raises the *active valence* of the metal from zero to some finite value: $2Cu^0 + O_2^0 \rightarrow 2Cu^{II}O^{II}$. *Metallic* copper has *no valence in use*. In CuO or $CuCl_2$ it has become bivalent. The copper has been oxidized. Similarly, changing $FeCl_2$ into $FeCl_3$ increases the active valence of the iron from two to three (oxidation). Conversely, changing $2HCl$ to Cl_2 decreases the active valence of chlorine from one to zero (oxidation).

Again, in displacement, *e.g.*, $Zn + 2HCl \rightarrow ZnCl_2 + H_2$, the zinc is oxidized because the active valence goes from zero to two, and the hydrogen is reduced.

Hence, **oxidation** consists in **increasing the active valence of a positive element or decreasing that of a negative element.** Reduction is the converse.

This way of stating the rule makes it clear why removing the elements of water is neither oxidation nor reduction. We are removing *both* a positive and a negative element, and are removing them in *equi-valent* amounts, $2H^I + O^{II}$.

Oxidation and Ionization. — If, in the last illustration, we write the equation ionically: $Zn + 2H^+ \rightarrow Zn^{++} + H_2$, we discover that, logically, we must consider the change from metallic zinc to zinc-ion to be in itself oxidation. This is the case whether the zinc-ion later combines with a negative ion to form a molecule or not. Mere union or disunion of ions is neither oxidation nor reduction. Conversely, the discharge of the $2H^+$ giving H_2 is reduction.

Thus, **ionization of an elementary substance to form a positive ion is oxidation,** and ionization to form a negative ion is reduction, and conversely.

Oxidation and Electrons. — Finally, since increasing the valence of a negative atom means adding one or more electrons to that atom, and increasing the positive valence of an atom means removing one or more electrons, we reach the *briefest* definition

by saying: **Oxidation is removing electrons and reduction is adding electrons.**

Making Equations for Oxidations and Reductions. — The writing of equations for actions involving oxidation and reduction, *where there are more than two substances on one side of the equation*, is difficult (compare p. 271), and a system or plan is of great value. The plan of **positive and negative valences** is most, generally applicable. In many cases, this plan may be much more neatly expressed in terms of **ions and electrons.**

Making Equations: Using Positive and Negative Valences. — 1. Each compound is composed of *elements* which are relatively to one another, *either positive or negative*. Thus, in $KMnO_4$, K and Mn are positive and O is negative.

2. *In each compound, the algebraic sum of the positive and negative valences must be zero.* This is simply the rule of equivalence (p. 128), with the addition of the idea of relative positiveness and negativeness.

This enables us **to determine the valence of each element in a compound like $KMnO_4$.** K is always univalent and positive. O, in inorganic compounds, is almost always bivalent and negative (among the few exceptions are those compounds in which oxygen atoms are in *direct* combination, as in hydrogen peroxide $H — O — O — H$). The valence of Mn has different values: $Mn^{II}Cl_2$, $Mn_2^{III}O_3$, $Mn^{IV}O_2$, $Mn_2^{VII}O_7$, etc. By the rule (sum of valences equals zero) we can tell, however, the valence of Mn in this compound. The total valence of $O_4 (4O^{II})$ is -8. That of K is $+1$. That of Mn must therefore be $+7$. Again, in $KClO_3$, the valence of O_3 is -6, that of K is $+1$, therefore that of Cl must be $+5$. Again, in H_2SO_4, the valence of O_4 is -8, that of H_2 is $+2$, and that of S must consequently be $+6$. Still again, in $K_2Cr_2O_7$, the valence of O_7 is -14, that of K_2 is $+2$, that of Cr_2 is therefore $+12$, and that of Cr necessarily $+6$.

3. Since rule 2 applies to every compound used or produced in a chemical change, it follows that when in a reaction *the valence of an element changes in value, that of one or more of the other elements must also change, so as to maintain the equality of $+$*

and — *valences.* Thus, if one element loses in valence, to the extent of $+6$, some other element (or elements) must *lose* -6, or *gain* $+6$. The gain (or loss) of one element must cancel the gain, (or loss) of some other element.

4. The *valence of a free element,* that is, its active valence, is *zero.* A free element is also *neutral* — neither positive nor negative — because it is not combined with any other element.

.. *Illustration of rules 3 and 4.* Thus, in the action for preparing chlorine with manganese dioxide (p. 178):

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2,$$

4H has the valence $+4$ on both sides. On the left side, 4Cl has the valence -4: on the right, 2Cl has the valence -2, and Cl_2 has the valence 0. So far as chlorine is concerned, there is a change from -4 to -2, or a difference of -2. Again, on the right, Mn has the valence $+2$, while on the left side it has the valence $+4$, a difference of $+2$. The two differences, -2 and $+2$, cancel one another. Stated otherwise, manganese lost $+2$ and chlorine lost -2, so that the other $+$ and $-$ valences *still in use* remained equal in number, and equi-valence was preserved.

Balancing an Equation. Suppose we wish to balance the equation for the preparation of bromine by the action of manganese dioxide and concentrated sulphuric acid on sodium bromide (p. 271). We ascertain, in the laboratory, that the products are free bromine, sodium-hydrogen sulphate, manganous sulphate and water.

Skeleton: $NaBr + MnO_2 + H_2SO_4 \rightarrow Br_2 + NaHSO_4 + MnSO_4 + H_2O.$
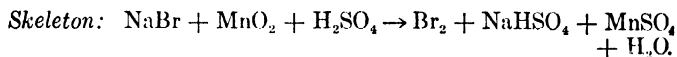
On examining the formulæ of the initial and resultant products in this equation, we find that *the valences of Br and Mn only have been affected.* On the left side, the valences of these elements are -1 and $+4$ respectively. On the right side, their valences have been changed to 0 and $+2$. Every bromine atom concerned in the reaction therefore loses in valence by — 1, and every atom of manganese loses in valence by $+2$. In order to maintain equality of $+$ and — valences, it is obvious that twice as many bromine atoms as manganese atoms must be involved,

We may therefore start to complete our equation by writing
$2NaBr$ in place of $NaBr$. This immediately requires the use of
$2NaHSO_4$ on the right side of the equation, in order to balance
up the sodium atoms. Our equation thus reads:

Incomplete: $2NaBr + MnO_2 + H_2SO_4 \rightarrow Br_2 + 2NaHSO_4 + MnSO_4 + H_2O.$
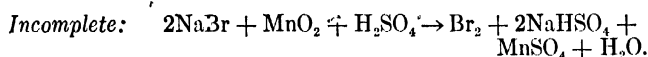
When we now count the number of sulphur atoms on the two
sides, we see that we need to write $3H_2SO_4$ on the left to obtain
equality. Having made this change, we have to write $2HO_2O$ on
the right, and then the quantities of all the elements present are
correctly balanced. *Our equation is therefore complete.*

Balanced: $2NaBr + MnO_2 + 3H_2SO_4 \rightarrow Br_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$
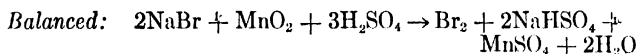
Balancing Another Equation. In the reaction for preparing
chlorine from potassium dichromate $K_2Cr_2O_7$ (p. 178), the
skeleton is:

Skeleton: $K_2Cr_2O_7 + HCl \rightarrow H_2O + KCl + CrCl_3 + Cl_2.$
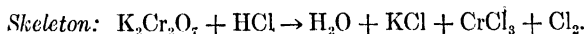
Here, in $K_2Cr_2O_7$, the valence of Cr is $+6$. In $CrCl_3$ it is
$+3$, a loss of $+3$. The chlorine also changes its valence from
-1 to 0, a loss of -1. Evidently, so that the changes may cancel
out, for every atom of Cr losing $+3$, 3 atoms of Cl must lose
3×-1 and be liberated:

Incomplete: $K_2Cr_2O_7 + HCl \rightarrow H_2O + 2KCl + 2CrCl_3 + 3Cl_2.$
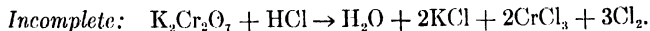
Since there is now, altogether, 14Cl on the right, 14HCl will be
required on the left. The 14H will give $7H_2O$.

Balanced: $K_2Cr_2O_7 + 14HCl \rightarrow 7H_2O + 2KCl + 2CrCl_3 + 3Cl_2.$
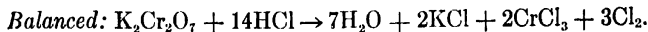
Making Equations by Means of Ions and Electrons. — All
oxidation reactions involving electrolytes can be written in terms
of ions. Thus, the oxidation of hydrochloric acid by potassium
permanganate can be so written. Potassium permanganate ion-
izes in solution to give the positive ion K^+ and the complex
negative ion $(MnO_4)^-$. The potassium-ion clearly is not affected,

and may be omitted. The substances actually concerned (see p. 177) are:

$$MnO_4^- + H^+ + Cl_2^- \rightarrow H_2O + Mn^{++} + Cl_2^0.$$
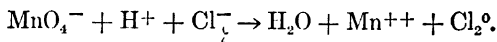
Cl_2^0 with no charge stands for free chlorine. Now we can divide the action into (1) the fate of the oxidizing agent and (2) the fate of the substance being oxidized.

The fate of the oxidizing agent, since all the Mn in the MnO_4^- goes to Mn^{++} and all the O_4 goes to H_2O, in the formation of which $8H^+$ will evidently be required, is expressed by the equation:

Skeleton: $\quad MnO_4^- + 8H^+ \rightarrow Mn^{++} + 4H_2O.$
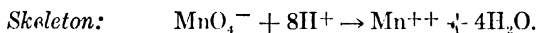
This equation is already balanced, so far as the atoms of the various elements present are concerned, but when we examine the electrical charges on either side, we find that there is a deficiency of 7 equivalents of negative electricity on the left hand, and a deficiency of only 2 equivalents of negative electricity on the right. In the course of the reaction, therefore, each equivalent of the oxidizing agent has gained $7 - 2 = 5$ equivalents of negative electricity. In other words, *each unit of MnO_4^- has gained five electrons* (p. 267). The true balanced equation is, consequently:

Balanced: $\quad MnO_4^- + 8H^+ + 5 \ominus \rightarrow Mn^{++} + 4H_2O.$ $\qquad$ (1)
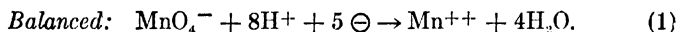
We understand where these electrons came from when we consider the fate of the chlorine. The change from Cl^- to Cl_2 may be expressed:

$$2Cl^- \rightarrow Cl_2^0 + 2 \ominus. \qquad (2)$$

In order to balance out the electrons in equations (1) and (2), we evidently require to multiply equation (1) by 2 and equation (2) by 5 throughout. When we do this, and add the two equations together in order to represent both the reduction of the manganese and the oxidation of the chlorine in a single equation, we obtain the final answer to our problem in the statement:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2^0.$$
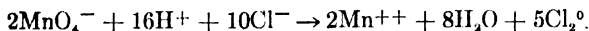
The student should compare this with the equation previously deduced on p. 177, and convince himself of their essential identity. , The chief advantages of the above method are as follows: (a)• the final equation contains only substances which have *actually undergone a change* in the reaction; (b) equations (1) and (2) represent *the oxidation and reduction reactions which actually occur at the electrodes* when the experiment is conducted in a battery-cell as a source of electrical energy (see p. 196); and (c) the method does not lead to incorrect results in the case of "trick" compounds such as H_2O_2. The representation is, therefore, more accurate from a practical view-point, and at the same time it furnishes us with a much clearer idea of the mechanism of electrochemical reactions. Additional examples of the application of this method to complex oxidation-reduction reactions will be presented for the student to solve in subsequent chapters.

The student is apt to underestimate the importance of the above sections, because he thinks that he can memorize the reactions discussed, or balance them by repeated trials, with less difficulty than is involved in the mastery of the recommended methods. He should recognise, however, that these methods are going to be of continuous service to him throughout the rest of his chemical career. It took longer to build a railroad from New York to San Francisco than it would have taken to walk the same distance, but that is no valid argument against the use of railroads.

Exercises. — 1. What volume of ozone will be taken up by 100 c.c. of water at 12° from a stream of oxygen containing 7.5 per cent of ozone (pp. 157, 287)?

2. At what temperature (approximately) will an aqueous solution of hydrogen peroxide, containing 17 g. of the substance to 1000 g. of water, freeze (pp. 291-292)?

3. Write the thermochemical equation for the oxidation of indigo by hydrogen peroxide (pp. 289, 293).

4. What volume (at 0° and 760 mm.) of oxygen would be obtained by the decomposition of the hydrogen peroxide in 1 kilogram of the 3 per cent solution?

5. Why does a given weight of chlorine in the form of hypo-chlorous acid have twice as great a bleaching (or oxidizing) capacity as has the same weight of chlorine in chlorine water?

6. How should you make pure potassium hypochlorite from chlorine-water?

7. Classify the following changes as oxidations or reductions: (a) $H_2Cr_2O_7 \rightarrow H_2CrO_4 + CrO_3$; (b) $HMnO_4 \rightarrow MnO_2$; (c) $I_2 \rightarrow 2I^-$; (d) $2H_2O_2 \rightarrow 2H_2O + O_2$; (e) $Zn \rightarrow Zn^{++}$.

8. Apply the positive and negative valence method of writing equations to the action of HCl on $KMnO_4$.

9. Apply the ion and electron method of writing equations to (a): the action of manganese dioxide and concentrated sulphuric acid on sodium bromide; (b) the action of HCl on $K_2Cr_2O_7$.

CHAPTER XXI

THE chief subjects of practical importance touched upon in this chapter are connected with potassium chlorate $KClO_3$ and perchlorate $KClO_4$. Hence our attention will be largely directed to the modes of making these substances and to their relations to one another. Incidentally, we shall encounter several actions of a complex and, to us, more or less novel kind.

Compounds of Chlorine Containing Oxygen. — The following are the names and formulæ of the parent substances:

HClO Hypochlorous acid, Cl_2O Hypochlorous anhydride,
[$HClO_2$] Chlorous acid, ...
. . . . ClO_2 Chlorine dioxide,
$HClO_3$ Chloric acid, ...
$HClO_4$ Perchloric acid, Cl_2O_7 Perchloric anhydride.

There are also salts of these acids, like the two substances mentioned in the first paragraph. Chlorous acid is itself unknown, but potassium chlorite $KClO_2$ and some other derivatives have been made.

The two anhydrides (p. 83), when brought into contact with water, combine with it to form the acids opposite which they stand in the table. Chlorine dioxide, however, is not related to any one acid in this way.

All these compounds differ from most that we have hitherto discussed, inasmuch as not one of them can be made by direct union of the simple substances.

Nomenclature. — The acids and salts *within one group* are distinguished by the terminations of, and prefixes to, their names. Thus we have:

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*Hydro*chlor*ic* acid	HCl	Sodium chlor*ide*	NaCl
*Hypo*chlor*ous* acid	HOCl	Sodium *hypochlorite*	NaOCl
Chlor*ous* acid	HClO$_2$	Sodium chlor*ite*	NaClO$_2$
Chlor*ic* acid	HClO$_3$	Sodium chlor*ate*	NaClO$_3$
*Per*chlor*ic* acid	HClO$_4$	Sodium *per*chlor*ate*	NaClO$_4$

The proportion of oxygen to the other elements is at the basis of the system. The terminations *ous* and *ite* indicate less oxygen than *ic* and *ate*. The prefix *hypo* (Greek, *below*) implies still less oxygen, the prefix *hydro* implies none at all. The *per*-acid contains the most oxygen.

It should be noted, however, that the use of *ic* and *ous* for more and less oxygen, respectively, and of *hypo* for still less and of *per* for still more oxygen are simply relative terms *within a single group*. Thus, sulphur*ic* acid H$_2$SO$_4$ has a composition entirely different from chlor*ic* acid, and both of these differ in composition from phosphor*ic* acid H$_3$PO$_4$. The names and formulæ of each group must be learned, separately.

The properties of hypochlorous acid and of hypochlorites have already been considered in detail in the preceding chapter.

Chlorates. — Like hypochlorous acid itself (p. 294), the hypochlorites are readily converted, in part, into chlorates. Thus, when chlorine is passed into a *warm*, concentrated solution of potassium hydroxide, and particularly when an excess of chlorine is used, the potassium hypochlorite changes into **potassium chlorate** KClO$_3$ as fast as it is formed. Since this action (equation 2) requires 3KClO, the equation formerly given (p. 296) must be tripled:

$$3Cl_2 + 6KOH \rightarrow 3KCl + 3KOCl + 3H_2O. \qquad (1)$$
$$3KOCl \rightarrow 2KCl + KClO_3 \qquad (2)$$

Adding: $\overline{3Cl_2 + 6KOH \rightarrow KClO_3 + 5KCl + 3H_2O.}$
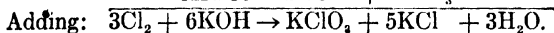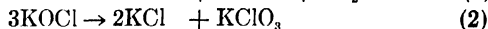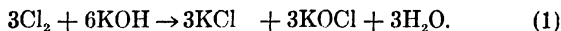
When the solution is cooled, the less soluble chlorate crystallizes.

This action involves converting five-sixths of the valuable potassium hydroxide into the relatively less valuable potassium chloride. Hence, in practice, the makers carry out the corresponding action with calcium hydroxide. They then add potas-

sium chloride to the resulting solution, containing calcium chloride (very soluble) and **calcium chlorate** $Ca(ClO_3)_2$. The potassium chlorate, formed by double decomposition, crystallizes when the solution is cooled.

All chlorates are at least moderately soluble in water (see Table inside of front cover). Potassium chlorate is used in making fireworks, explosives, and matches. An intimate mixture with sugar $C_{12}H_{22}O_{11}$ burns with semi-explosive violence, the oxygen of the salt combining with the carbon and hydrogen of the sugar to form carbon dioxide and water.

Chloric Acid $HClO_3$.—Since none of the acids of this series can be obtained by direct union of their elements (p. 307), it is usual first to prepare the salts, and to make the acids from the salts by double decomposition. This acid may be obtained, in solution in water, by adding the calculated amount of diluted sulphuric acid to a solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \leftrightarrows BaSO_4 \downarrow + 2HClO_3.$$
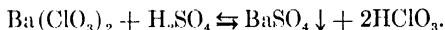
The barium sulphate, being insoluble, is removed by filtration. It will be noted that double decomposition involving **precipitation may** thus **be used for obtaining a soluble product,** as well as an insoluble one (compare selenic acid, p. 353).

The solution may be concentrated (to about 40 per cent) by evaporation, but must not be heated above 40°, as the acid decomposes near this temperature. The resulting thick, colorless liquid has powerful oxidizing qualities, setting fire to paper (made of cellulose $(C_6H_{10}O_5)_y)$ which has been dipped into it. It converts iodine into iodic acid, $2HClO_3 + I_2 \rightarrow 2HIO_3 + Cl_2$. When not in solution, or when warmed in solution beyond 40°, the acid decomposes, giving **chlorine dioxide** and **perchloric acid:**

$$3HClO_3 \rightarrow H_2O + 2ClO_2 + HClO_4.$$

Chlorine Dioxide: Chlorous Acid.— Chlorine dioxide ClO_2 (see above) is a yellow gas which may be liquefied, and boils at $+ 10°$. The gas and liquid are violently explosive, the substance being resolved into its elements with liberation of much heat. It is formed whenever chloric acid is set free, and hence it is seen

when a little powdered potassium chlorate is touched with a drop of concentrated sulphuric acid (end of last section).* Concentrated hydrochloric acid turns yellow from the same cause when any chlorate is added to it. These actions are used as **tests** for chlorates, and distinguish them from perchlorates. ₌With water, chlorine dioxide gives a mixture of **chlorous acid** $HClO_2$ and chloric acid, and with bases ₚ mixture of the **chlorite** and chlorate.

₁ **Perchlorates.** — When heated, chlorates give **perchlorates.** Chlorates also give oxygen at the same time (p. 31):

$$\begin{cases} 2KClO_3 \rightarrow 2KCl + 3O_2, \\ 4KClO_3 \rightarrow 3KClO_4 + KCl. \end{cases}$$
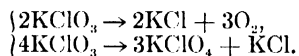
These actions, like the three decompositions of hypochlorous acid (p. 294), are independent, and proceed simultaneously. They are **concurrent** reactions (see below). Their relative speed, however, varies with the temperature, and the decomposition into chloride and oxygen may completely outrun the other when a catalytic agent like manganese dioxide is added (p. 32). When pure potassium chlorate is heated cautiously, about one-fifth of it has lost all its oxygen by the time the rest has turned into perchlorate. The mixture may be separated by grinding with the minimum quantity of water which will dissolve the chloride it contains. The perchlorate, having at 15° less than one-twentieth of the solubility of the chloride, will remain, for the most part, undissolved. The perchlorates are much more stable (p. 43) than the chlorates, or hypochlorites: they are all soluble in water, and they are **used** in making matches and fireworks.

Perchloric Acid $HClO_4$ and Perchloric Anhydride Cl_2O_7. — Pure **perchloric acid** explodes when heated above 92°. But, like other liquids, its boiling-point is lower when its vapor *is under reduced pressure* (compare p. 76). At 56 mm. pressure it boils at 39°, a temperature at which hardly any decomposition is noticeable. Hence the acid may be made by passing HCl gas through

---

* The mixture of sugar and potassium chlorate (p. 309) can be set on fire by a drop of sulphuric acid. The latter liberates chloric acid, which in turn gives ClO_2, and the latter, being a violent oxidizing agent, starts the combustion of the sugar.

a saturated solution of sodium perchlorate, decanting off the clear liquid from the precipitate of less soluble sodium chloride that is formed (compare p. 309), and distilling cautiously under a low pressure (p. 291):

$$NaClO_4 + HCl \rightleftarrows NaCl \downarrow + HClO_4.$$
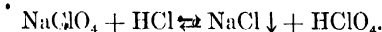
Perchloric acid is a colorless liquid, which decomposes, and often explodes spontaneously, when kept. A 70 per cent solution in water is perfectly stable, however. Although it is an active oxidizing agent, it is not so active as chloric acid, and does not oxidize hydrogen chloride in cold aqueous solution. Hence a drop of hydrochloric acid placed on a crystal of a perchlorate gives no yellow color. When the acid is liberated by concentrated sulphuric acid, it does not at once give the yellow chlorine dioxide (p. 309).

Perchloric anhydride Cl_2O_7 may be prepared by adding phosphoric anhydride to perchloric acid in a vessel immersed in a freezing mixture, $P_2O_5 + 2HClO_4 \rightarrow 2HPO_3 + Cl_2O_7$. Phosphoric anhydride is often used in this way for removing the elements of water from compounds. It combines with the water to form metaphosphoric acid HPO_3. By gently warming the mixture, the perchloric anhydride can be distilled off. It is a colorless liquid boiling at 82° (760 mm.) and exploding when struck or too strongly heated.

Relation of Anhydride and Acid or Salt. — The derivation of the formula of the anhydride from that of the acid or salt should receive special attention. In the mind of the chemist, the one always instantly suggests the other, so often does he think of them as potentially the same substance. The beginner, however, finds this habit hard to acquire, and indeed is more likely to blunder, in trying to divide the formula of an acid into the formulæ of water and the anhydride, than in any other calculation he makes.

The rule is: If the formula of the acid shows an *even* number of hydrogen atoms (H_2SO_4 or H_4SiO_4), subtract all the elements of water (H_2O or $2H_2O$), and the balance is the anhydride (SO_3 or SiO_2). The divided formulæ are H_2O,SO_3 or $2H_2O,SiO_2$. If

there is an *odd* number of hydrogen atoms ($HClO_4$ or H_3PO_4) *double* the formula ($H_2Cl_2O_8$ or $H_6P_2O_8$), and subtract all the elements of water as before (Cl_2O_7 or P_2O_5). Then check the result, by adding the water again, and dividing by two, correcting the blunder if one has been made.

If the substance is a salt ($CuSO_4$ or $KClO_4$), subtract the oxide of the metal (CuO or K_2O), taking care to assign to the metal the same valence in the oxide as it shows in the salt.

Concurrent and Consecutive Reactions. — When two or more reactions go on simultaneously in the same materials, the actions may be consecutive (see below) or they may be parallel. In the latter case they are called **concurrent reactions**. Thus, hypochlorous acid undergoes three different changes:

$$2HClO \rightarrow H_2O + Cl_2O.$$
$$3HClO \rightarrow HClO_3 + 2HCl.$$
$$2HClO \rightarrow 2HCl + O_2.$$
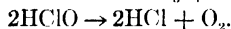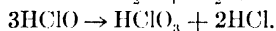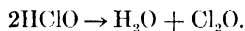
Some molecules decompose into water and chlorine monoxide (p. 294), while others give chloric acid and hydrogen chloride, and still others hydrogen chloride and oxygen. Since the *same molecule* cannot undergo more than one of these different changes, it follows that the actions are independent of one another. This is shown by the fact that in sunlight the third predominates, while in the dark it falls far behind the second. Since the *relative* quantities of the products vary, the **several simultaneous actions cannot be put in the same equation.** The fundamental property of an equation is to show the *constant* proportions by weight between every pair of substances in it. Hence three separate equations are required in the present, and in all similar cases where all the proportions are not constant. Thus, again, in the decomposition of potassium chlorate by heating (p. 310), it would be misleading and wrong to add the two equations together and write, for the whole action:
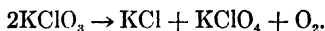
$$2KClO_3 \rightarrow KCl + KClO_4 + O_2.$$

This equation would mean that the proportions amongst the products were always $KCl : KClO_4 : O_2$ or $74.56 : 138.56 : 32$.

whereas, in fact, the proportions vary with the conditions — the temperature used or the presence of a catalyst which hastens one action but not the other.

Consecutive reactions, however, like (1) followed by (2) on pp. 295, 308, may be combined in one equation, since in them all the proportions must necessarily be constant. These equations are interlocked, for (2) consumes what (1) produces.

Oxygen Acids of Bromine. — No oxides of bromine have been made, but the acids HOBr (hypobromous acid) and $HBrO_3$ (bromic acid) and their salts are familiar.

By the action of bromine on dilute, cold potassium hydroxide solution, **potassium bromide** and **hypobromite** are formed:

$$Br_2 + 2KOH \rightarrow KBr + KOBr + H_2O.$$

When the solution is heated, the hypobromite turns into **potassium bromate** and bromide. The actions are exact parallels of the corresponding ones for the hypochlorite (pp. 295, 308).

Aqueous **bromic acid** $HBrO_3$ may be made in the same way as chloric acid (p. 309). The solution is colorless and has powerful oxidizing properties. Thus, it converts iodine into iodic acid: $2HBrO_3 + I_2 \rightarrow 2HIO_3 + Br_2$. It appears, therefore, that iodine has more affinity for oxygen than has bromine.

The Oxide and Oxygen Acids of Iodine. — There is one oxide, iodic anhydride I_2O_5. This, dissolved in water, gives iodic acid, HIO_3. **Sodium iodate** $NaIO_3$ is found in Chile saltpeter. Hypo-iodites and per-iodates are also known.

Iodic acid HIO_3 is more readily formed by passing chlorine through iodine suspended in water:

$$5HOCl + H_2O + I_2 \rightarrow 2HIO_3 + 5HCl.$$
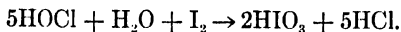
A still better way is to boil iodine with aqueous nitric acid HNO_3 (see p. 397). The latter gives up oxygen readily, and is here reduced to nitric oxide NO:

$$3I_2 + 10HNO_3 \rightarrow 6HIO_3 + 10NO + 2H_2O.$$

(The student should try himself out upon both of the above equations by the methods indicated on pp. 301-305, starting

with the skeletons as in Exercise 9, p. 315). In both these actions the initial substances (including the excess of nitric acid) and the products, with the exception of the iodic acid itself, are all volatile. When the solution is concentrated by evaporation, therefore, only the iodic acid crystallizes. It is a white solid, perfectly stable at ordinary temperatures, and can be kept indefinitely. At 170° it begins to give off water vapor $(2HIO_3 \rightleftarrows H_2O + I_2O_5)$, leaving **iodic anhydride**. The latter is a white crystalline powder which may be raised to 300° before it, in turn, breaks up, giving iodine and oxygen.

Chemical Relations. — The compounds of the halogens with metals and with hydrogen diminish in stability, with ascending atomic weight of the halogen. Each halogen will displace those following it from *this kind* of combination. In the case of the oxygen compounds, the order of stability is just the reverse, those of iodine, for example, being the only ones which are reasonably stable.

Amongst the oxygen acids of any one halogen, those containing most oxygen are most stable. The salts are in all cases more stable by far than the corresponding acids.

The halogens when combined with metals and hydrogen are univalent (HI, KCl, etc.). It is clear, however, that, when united with oxygen, their valence is usually higher. The maximum is shown in perchloric anhydride (Cl_2O_7), where chlorine appears to be septivalent.

The formulæ of the acids might be written so as to retain the univalence:

$$H - Cl, \ H - O - Cl, \ H - O - O - Cl, \ H - O - O - O - Cl,$$
$$H - O - O - O - O - Cl.$$
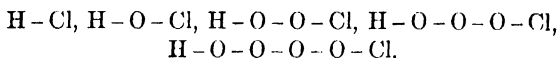
But compounds in which we are *compelled* to believe that two oxygen units are united are usually unstable (*e.g.*, hydrogen peroxide, $H - O - O - H$), and we should expect the instability would be greater with three and with four units of oxygen in combination. Here, however, the reverse state of affairs must be taken account of in our formulæ, for $HClO_4$ is the most stable of the chlorine set. This reasoning, together with the septivalence

in Cl_2O_7, leads us to assume the valence seven in perchloric acid (see Periodic system). The structural formulæ (see p. 350) of some of these substances are therefore written as follows:

$$H-Cl, \quad H-O-Cl, \quad H-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cl}}=O, \quad Na-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{I}}=O.$$
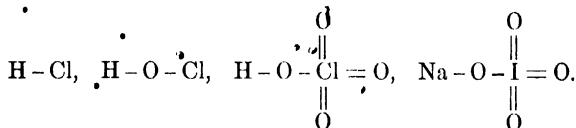
• **Exercises.** — 1. Assign to its proper class (p. 168) each of the actions mentioned in this chapter.

2. Knowing that potassium fluosilicate K_2SiF_6 is insoluble, how should you make chloric acid (p. 309)?

3. Make the equation for the interaction of chlorine with calcium hydroxide in hot water (p. 308). How should you make zinc chlorate from zinc hydroxide $Zn(OH)_2$?

4. On what circumstances would the possibility of making barium chlorate by action of chlorine on barium hydroxide depend (p. 309)? Could pure barium chlorate be obtained easily by this means (see Table of Solubilities)?

5. Make the equations for: (a) the preparation of potassium bromate; (b) pure aqueous bromic acid; (c) the interaction of iodine with aqueous potassium hydroxide in the cold, and (d) when heated.

6. Make the equations for the interactions of chlorine dioxide with water, and with aqueous potassium hydroxide.

7. Find the formulæ of the anhydrides of the following acids: HPO_3, H_2SeO_4, H_3AsO_3, H_3AsO_4, H_6SO_6.

8. Find the formulæ of the anhydrides of the acids from the following formulæ of salts: Na_2SiO_3, Na_2HPO_4, NaH_2PO_3, $Na_2H_3IO_6$.

9. Apply each of the two methods (pp. 301-305) of writing complex equations to balance the following skeleton reactions:

(a) $HClO_3 \rightarrow H_2O + ClO_2 + HClO_4$.

(b) $KClO_3 \rightarrow KClO_4 + KCl$.

(c) $HOCl + H_2O + Br_2 \rightarrow HBrO_3 + HCl$.

(d) $HBrO_3 + I_2 \rightarrow HIO_3 + Br_2$.

(e) $I_2 + HNO_3 \rightarrow HIO_3 + NO + H_2O$.
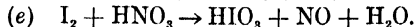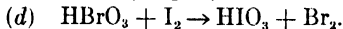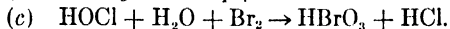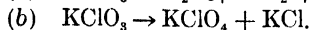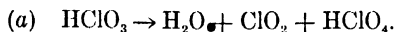
CHAPTER XXII

SULPHUR AND HYDROGEN SULPHIDE

SULPHUR, the compounds of which have been so often mentioned, provides us, in sulphuric acid, with a substance which has more extensive and more important applications in commerce than any other chemical. The element sulphur, itself, enters, with potassium nitrate and charcoal, into gunpowder. Vulcanite is a compound of caoutchouc (rubber) and sulphur. Sulphur is employed to destroy fungi on grape-plants, and furnishes sulphur dioxide for bleaching and disinfecting, as well as for use in paper manufacture.

Sources. — The greater part of the sulphur of commerce comes from Sicily, Louisiana and Texas. In Sicily, free sulphur is mixed with pumice and other rocks. When the lumps of rock, obtained by mining or quarrying, are heated by setting fire to the sulphur (there is no coal in Italy), the sulphur melts and runs to the bottom of the kiln. This product is far from pure, and is distilled from iron retorts. The vapor is condensed in chambers of brick, and the liquid is run into moulds, giving **roll sulphur.** The first vapor condensed, while the chambers are cold, yields **flowers of sulphur.**

In Louisiana the sulphur occurs in a deposit over half a mile in diameter, below 900 feet of clay, quicksand, and rock. It is obtained by means of borings, which permit four pipes, one within the other, to reach the deposit. Water, previously heated under pressure to a temperature of 170°, is pumped down the two outside pipes (6 and 8 inches in diameter). After time has been allowed for the melting of a quantity of the sulphur (it melts at 114.5°), compressed air is pumped down through an inner, one-inch pipe. The melted sulphur, alone, has twice the specific

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gravity of the water in the outer pipes. But the air breaks up into small bubbles, forming with the liquid sulphur an emulsion which has a lower specific gravity, and this flows freely up a three-inch pipe which surrounds the air pipe (see Fig. 83). The sulphur runs into wooden enclosures, measuring 150 by 250 feet,

in which it quickly solidifies. The product is so pure that, for most purposes, no other treatment is required. The output of Louisiana and Texas — 500 tons a day from each well and, in all, over 1,000,000 tons annually — supplies the whole demand of the United States, and could easily be increased.

A number of sulphates, such as gypsum ($CaSO_4,2H_2O$) and barite ($BaSO_4$), and several sulphides, such as galena (PbS), zinc blende (ZnS), and pyrite (FeS_2), are found in large quantities as minerals. The last two sulphides are used in the manufacture of sulphuric acid.

Fig. 83.

Allotropic Forms of Sulphur.

— Sulphur appears in two different liquid forms, and in two familiar and perfectly distinct solid varieties. The two latter are called, from their crystalline forms, **rhombic** and **monoclinic** sulphur.

Physical Properties of Rhombic Sulphur.

— This form is yellow, with *specific gravity* 2.06. Natural sulphur, roll sulphur, and practically all of most specimens of flowers of sulphur are of this variety, and are identical in all physical properties. Specimens of natural sulphur often show the rhombic crystalline form very clearly. All the forms of sulphur are *insoluble* in water, and
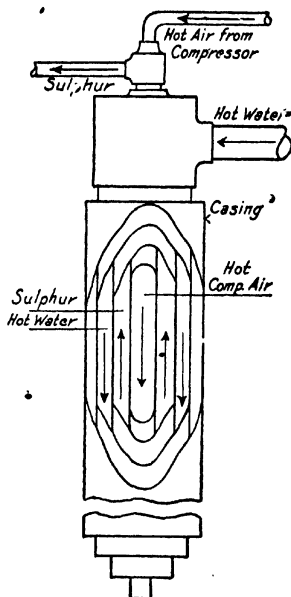
all the crystalline forms are *soluble* in carbon disulphide. Good rhombic crystals are obtained from the solution (Fig. 10, p. 18).

The rhombic form is stable when not heated above 96°. If kept above this temperature, it changes into monoclinic sulphur.

Monoclinic Sulphur. — This form is obtained most quickly by first melting some sulphur (m.-p. 114.5°), and then allowing it slowly to cool. As the temperature is now above 96°, the crystals which grow in the liquid are of the monoclinic variety. They are long, transparent, pale-yellow needles (Fig. 84), almost rectangular in section, and bevelled at the points. The specific gravity is 1.96. This form can be kept indefinitely above 96°, but, when allowed to cool below that temperature, it slowly becomes opaque, changing into particles of rhombic sulphur.

The temperature at which a substance changes its crystalline form is called a *transition point*. It is analogous to the fusion point in the case of a solid and a liquid; only at this one point can both forms exist together in equilibrium.

Fig. 84.

The Two Liquid Forms: Amorphous Sulphur. — When sulphur is melted, and the liquid is heated, two fluid, mutually soluble forms of sulphur are produced. These are known as S_λ and S_μ or amorphous sulphur. As the temperature rises, the second variety increases in quantity at the expense of the first variety. When the temperature is lowered, the reverse change occurs:

$$S_\lambda \rightleftarrows S_\mu \text{ (amorphous)}.$$
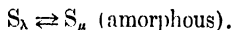
If the temperature is lowered gradually, therefore, only monoclinic sulphur (by crystallization of the S_λ) is obtained, the reaction proceeding to completion in the reverse direction owing to the removal of S_λ (compare p. 213). But the change from S_μ to S_λ takes place only very slowly, except at temperatures near the boiling-point. Consequently, if the liquid is quickly chilled, by pouring into a cold vessel or into cold water, the S_μ is found as a non-crystalline substance mixed with the crystalline form. The crystalline form can be dissolved out with carbon disulphide,

leaving the **amorphous sulphur** which is not soluble. The proportion of S_μ varies from 3.6 per cent at 120°, to 11 per cent at 160° and about 34 per cent at 445° (the boiling-point of sulphur). S_μ is very viscous, so that, as its quantity increases, the whole liquid becomes thick. At 120° molten sulphur is a pale-yellow, limpid fluid, at 260° a vessel containing it can be inverted without loss of the dark-brown viscous material.

Amorphous sulphur is a *super-cooled liquid*, and not a true solid, for true solids are all crystalline (see p. 106). At room temperature it changes into rhombic sulphur, but so slowly that the transformation even of a small part of it can be detected (by treating with carbon disulphide) only after the lapse of many months. At 100° the change is complete in less than an hour (compare p. 215).

Elastic sulphur. — When melted sulphur is chilled, the amorphous sulphur does not at once become hard. Sulphur which has been heated to a high temperature, therefore, and then suddenly cooled, consists at first of a sticky, transparent, elastic material, called **elastic or plastic sulphur.** In the course of forty-eight hours, however, this becomes opaque and hard, because of the separation of the crystalline and the hardening of the amorphous varieties.

Melting and Freezing-Points. — Amorphous sulphur, like glass and other amorphous substances, softens when heated, but has no sharp melting temperature. The two crystalline forms have different melting-points, rhombic melting to form S_λ at 112.8°, and monoclinic at 119.25°. But these are difficult to observe, as the rhombic begins to turn into monoclinic above 96°, and gradual transformation of S_λ to S_μ, to produce an equilibrium mixture of the two, occurs in both cases in the liquid state. Hence, the only temperature which is easy to observe is that at which both the solid forms melt when heated *very slowly*, and that at which the liquid freezes if cooled very slowly, namely 114.5°. This is the so-called *natural freezing-point* of sulphur.

Chemical Properties. — The vapor density of sulphur indicates that the vapor is a mixture of the molecules S_8, S_6 and S_2,

the former diminishing and the latter increasing in number as the temperature is raised (see p. 122).

All the *metals,* excepting gold and platinum, *combine* with sulphur to form sulphides, and in most cases much heat is given out during the union. Sulphur unites with *chlorine* to give sulphur monochloride S_2Cl_2, used in vulcanizing rubber, and burns in *oxygen* to give sulphur dioxide: *

$$S + O_2 \rightarrow SO_2.$$
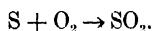
In these compounds the *valence* of an atomic weight of sulphur appears to be one (in S_2Cl_2) or four (in SO_2). These are exceptional values, however, the common valences being two (in H_2S, ZnS, etc.) and six (in SO_3, SO_2Cl_2, etc.).

Moist sulphur is slowly *oxidized* at ordinary temperatures to sulphuric acid:

Skeleton: $S + H_2O + O_2 \rightarrow H_2SO_4.$
Balanced: $2S + 2H_2O + 3O_2 \rightarrow 2H_2SO_4.$
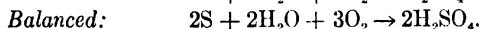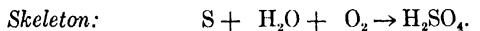
In the equations, the simple formula S is used in place of a molecular formula. The latter is needed only when questions about the volume of the vapor are asked, and sulphur is almost always used only in solid or melted form. Then, too, the vapor contains several kinds of molecules, and using S_8 or S_6 would introduce large and inconvenient coefficients.

HYDROGEN SULPHIDE H_2S

This gas is found dissolved in some mineral waters, which in consequence are known as sulphur waters. It is produced in the decomposition of animal matter containing sulphur (proteins), when air is excluded. Hence the odor of rotten eggs is due in part to its presence.

Preparation. — 1. Hydrogen and sulphur do not unite perceptibly in the cold. At 310° almost complete union occurs, but about seven days are required for the attainment of equilibrium.

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* Traces of sulphur trioxide are found at the same time. They **give** minute drops of sulphuric acid, which cause a haziness in the **gas when it is** formed by this action.

2. Sulphides of metals, being salts, are acted upon more or less easily by dilute acids, and give hydrogen sulphide. Ferrous sulphide, the least expensive of those easily affected, is generally used:

$$FeS + 2HCl \rightleftharpoons H_2S \uparrow + FeCl_2.$$
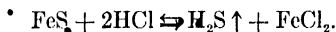
The action, like all double decompositions, is reversible. But use of an excess of hydrochloric acid forces it forward, and the escape of the gaseous hydrogen sulphide reduces the backward action almost to zero. The gas can be made in a flask fitted like that in Fig. 30 (p. 62), or in a Kipp's automatic generator (Fig. 32). It can be collected by upward displacement.

3. Hydrogen sulphide is the invariable product of the extreme reduction of any sulphur compound. Thus, it is formed by the action of hydrogen iodide upon concentrated sulphuric acid (p. 278). Even sulphur itself is reduced by dry, gaseous hydrogen iodide:

$$2HI + S \rightarrow H_2S + I_2.$$
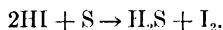
Physical Properties. — Hydrogen sulphide is a *colorless* gas with an *odor* recalling rotten eggs. It is rather easily *liquefied*, and the liquid boils at about $-60°$ and freezes at $-83°$. The density, implied in the formula H_2S, shows that the gram-molecular volume weighs 34.076 g., so that the density is about one-sixth greater than that of air. The gas is moderately *soluble* in water (290 vols. in 100 vols. water at 20°), a property which enables us to carry out many reactions of the gas upon substances in solution.

Physiological Properties. — Care must be taken to allow as little of the gas as possible to escape into the air, and all work with it should be done in a well-ventilated hood. The proportion must reach 1 part in 200 of air, however, before fatal results follow breathing the mixture. The best antidote is very dilute chlorine.

Chemical Properties. — **1.** The gas *burns* in the air, giving water and sulphur dioxide:

Skeleton: $H_2S + O_2 \rightarrow H_2O + SO_2.$
Balanced: $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2.$
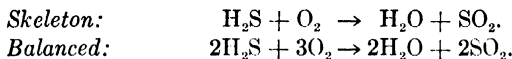
2. The compound is *not very stable.* When heated, for example, in the interior of its own flame, it is partially decomposed into free sulphur and hydrogen. A cold porcelain dish (Fig. 85) placed in the flame will condense some of the sulphur on its surface.
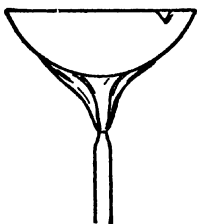
3. On account of its instability, and the ca:e with which it gives up hydrogen, the gas is a *reducing agent.* Thus, when jars of hydrogen sulphide and sulphur dioxide are placed mouth to mouth, a deposit of sulphur gradually appears:

FIG. 85. $SO_2 + 2H_2S \rightarrow 2H_2O + 3S.$
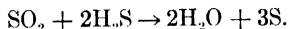
Part of the free sulphur found in nature seems to be liberated by the action of these gases, both of which are found in volcanic regions. The gases must be moist, for, without water vapor as a contact agent, no interaction occurs.

In this action the sulphur dioxide loses its oxygen. We say that the H_2S was *oxidized* by the SO_2, or that the SO_2 was *reduced* by the H_2S. As we have already noted, every reduction involves also an oxidation.

4. The metals, down to and including silver in the activity series, quickly receive a coating of sulphide when exposed to the gas:

$$2Ag + H_2S \rightarrow Ag_2S + H_2 \uparrow.$$
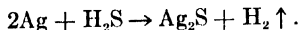
The tarnishing of silver in the household is due to the presence of a trace of hydrogen sulphide in the illuminating gas which escapes from slight leaks in the pipes.

Chemical Properties of the Aqueous Solution of Hydrogen Sulphide. — While the gas itself is not an acid, its solution in water gives a **feeble acid reaction** with litmus, and is sometimes named **hydrosulphuric acid.** The conductivity of a $N/10$ aqueous solution is small, and only 0.0007 (0.07 per cent) of the substance is ionized:

$$H_2S \leftrightarrows H^+ + HS^- \; (\rightleftarrows H^+ + S^=).$$

The second dissociation of the small amount of hydrosulphide-ion HS^- into H^+ and $S^=$ is almost negligible, and the amount of sulphide-ion $S^=$ present is therefore exceedingly minute.

As an acid, the solution of hydrogen sulphide may be neutralized by bases. For the same reason it enters into double decomposition with salts (see p. 329).

By the action of **oxygen** from the air upon an aqueous solution of hydrogen sulphide, the **sulphur is slowly displaced** and appears in the form of a fine white powder:

$$O_2 + 2H_2S \rightarrow 2S \downarrow + 2H_2O.$$
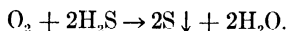
This is an action similar to the displacement of ionic bromine by free chlorine (p. 271).

The solution of the gas is a **reducing agent,** as its action upon iodine shows (p. 279). So, also, in presence of an acid, it removes oxygen from dichromic acid (produced by the action of an acid upon potassium dichromate):

$$K_2Cr_2O_7 + 8HCl + 3H_2S \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3S.$$
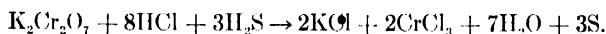
This is another good equation for the student to exercise his ingenuity upon, using the methods described in pp. 301-305 to balance it correctly. See exercise 8, p. 331.

Sulphides. — As a dibasic acid (p. 246), hydrogen sulphide gives both acid and normal (or "neutral") sulphides, such as NaHS and Na$_2$S. The names *acid* and *neutral*, as we shall see, refer here to the *constitution* of the compounds, not to the behavior of their solutions.

The **acid sulphides** (hydrosulphides) are obtained by passing the gas *in excess* into solutions of soluble bases:

$$H_2S + NaOH \rightleftarrows H_2O + NaHS,$$
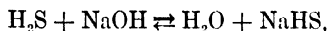
and give, in solution, a **very faintly alkaline** reaction. The reason for this will appear below (p. 325).

By adding to the above-mentioned solution an amount of sodium hydroxide equal to that used before, and driving off the

water by evaporation, the second unit of hydrogen is displaced, and normal ("neutral") sodium sulphide is formed:

$$NaOH + NaHS \leftrightarrows Na_2S + H_2O \uparrow .$$
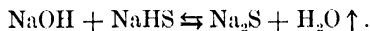
The solution of this salt in water is **strongly alkaline** in reaction. **In general, any normal salt derived from an active base and a weak acid** gives an **alkaline solution.** The explanation by the ionization theory is thus of general interest.

Water, it will be remembered, is ionized to a very small extent. When *any salt* is dissolved in water, therefore, there exists the possibility of a double decomposition taking place. Thus with sodium chloride:

$$NaCl \rightleftarrows Na^+ + Cl^-$$
$$H_2O \rightleftarrows OH^- + H^+$$
$$\qquad \updownarrow \qquad \updownarrow$$
$$\quad NaOH \quad HCl$$
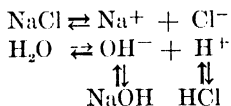
In this case, however, the extent of formation of NaOH and HCl is altogether negligible. NaOH and HCl are *both* very highly ionized in aqueous solution, their existence in appreciable amount would involve the presence of *both* OH⁻ and H⁺ in quantity, and these ions would immediately combine to form water.

When a salt like sodium sulphide is dissolved in water, the state of affairs is different, as may be seen by studying the arrows in the ionic equations:

$$Na_2S \rightleftarrows 2Na^+ + S^=$$
$$2H_2O \rightleftarrows 2OH^- + 2H^+$$
$$\qquad \updownarrow \qquad \updownarrow$$
$$\quad 2NaOH \quad H_2S$$
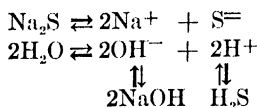
Double decomposition with the ions of water here involves the formation of some NaOH and some H₂S. Now the latter substance is an *exceedingly weak acid.* While, therefore, any NaOH formed is almost entirely ionized, furnishing OH⁻ to the solution, any H₂S formed remains, on the contrary, almost entirely in the non-ionized state. Now we have learned (p. 260) that one way of driving a reversible reaction to completion is to remove one product *as a non-ionized substance.* This reaction cannot be driven *to completion* in this way, since we have the **information**

of another practically non-ionized substance, water, tending to drive the reverse reaction to completion. In such circumstances, obviously, a balance must be struck between the two conflicting tendencies, and we will be left with a solution in which *partial* double decomposition has occurred. But such a solution will contain a much higher concentration of OH⁻ from the highly ionized NaOH than of H⁺ from the practically non-ionized H_2S. It will, therefore, react like an alkali.

Properties of Sodium Hydrosulphide Solution. — The faint alkalinity of a solution of this salt in water may also be understood by reference to the formulation given below.

$$\mathrm{NaHS} \rightleftarrows \mathrm{Na^+} + \mathrm{HS^-} : \rightleftarrows \mathrm{H^+} + \mathrm{S^=}$$
$$\mathrm{H_2O} \rightleftarrows \mathrm{OH^-} + \mathrm{H^+} :$$
$$\qquad \updownarrow \qquad \updownarrow \quad :$$
$$\qquad \mathrm{NaOH} \quad \mathrm{H_2S} \quad :$$
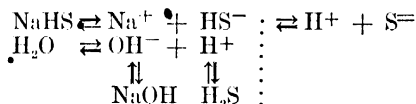
Restricting our attention at first to the equilibria represented to the *left* of the dotted line, we see that, just as in the preceding case of sodium sulphide, any double decomposition with the ions of water will result in the solution becoming alkaline. But there is here another factor to be taken into account. Sodium hydrosulphide, being a salt, is highly ionized into Na⁺ and HS⁻, and the latter ion, as we have seen above (p. 323), possesses a tendency, albeit extremely slight, to dissociate again into H⁺ and S⁼. If this tendency were at all pronounced, a solution of sodium hydrosulphide would necessarily react *as an acid*, owing to the H⁺ produced. It would be, in fact, true to its name, an *acid salt*. But here *the amount of H⁺ resulting from the dissociation of HS⁻ is so small that it does not quite equal the excess of OH⁻ resulting from the double decomposition between NaHS and H₂O.* There is therefore still a slightly greater concentration of OH⁻ than of H⁺ in the solution, and the solution consequently reacts very faintly alkaline.

It may be noted at this stage that the formulation given in the case of sodium sulphide above (p. 324) is not *strictly* accurate, since in the last vertical column a direct equilibrium between the ions 2H⁺ and S⁼ and the undissociated molecule H_2S is

postulated, whereas in point of fact combination of the ions takes place in two stages through the intermediate ion HS^-. The student will discover, nevertheless, if he formulates the action for himself in the two stages, that the same conclusion is thereby reached, and within the scope of this volume we shall find the abbreviated method of formulation employed on p. 324 not only sufficient for the present illustration, but also exceedingly useful in explaining many similar reactions in analytical chemistry which will come up for discussion later.

Hydrolysis of Salts. — The interaction of a salt with water is called **hydrolysis.** The action is the reverse of neutralization (p. 258), water and a salt giving, by double decomposition, an acid and a base. *The effect is noticeable,* however, only *when the acid and base are of very unequal activity.* **A salt which, by hydrolysis, gives an active base and a weak acid, furnishes a solution the reaction of which is basic.** Thus the solution of sodium carbonate in water reacts basic, because carbonic acid is a feeble acid.

Conversely, **if the salt gives, by hydrolysis, a weak base and an active acid, then the solution is acid in reaction.** Thus, the solution of cupric sulphate reacts acidic because cupric hydroxide is a feeble base.

The extent of hydrolysis, even in cases where it is distinctly observable, such as sodium carbonate and cupric sulphate mentioned above, is in general only small. Borax, a salt of an extremely weak acid (p. 456), reacts distinctly alkaline in water, but the degree of hydrolysis in a 0.1 N solution is only one-half of one per cent. The reason, of course, lies in the fact that water is very much less ionized even than most exceedingly weak acids like boric acid or most exceedingly weak bases like cupric hydroxide. The tendency towards the completion of *neutralization,* therefore, preponderates considerably in most cases over the tendency towards the completion of *hydrolysis.*

When we consider a salt of an *extraordinarily* weak acid or base, nevertheless, very extensive hydrolysis in solution must evidently occur. An example is immediately available in the case of sodium sulphide. The tendency towards the second stage of

ionization in H_2S, as expressed by the equation $HS^- \rightleftarrows H^+ + S^=$, is exceedingly slight. In other words, as a *dibasic acid* hydrosulphuric acid is *exceedingly weak*. It is, indeed, *even weaker than water*. In consequence of this, the degree of hydrolysis in a solution of "neutral" sodium sulphide is very high, and the solution reacts strongly alkaline. As a matter of fact, if we formulate the hydrolysis in strict detail in two stages, as suggested above, and consider the various equilibria quantitatively, we find that a decinormal solution of sodium sulphide in water at 25° is hydrolyzed to the extent of 86.4 per cent into sodium hydrosulphide and sodium hydroxide. The hydrolysis of sodium hydrosulphide, on the other hand, is relatively inappreciable. As a *monobasic acid*, hydrosulphuric acid, though ordinarily classed as a "weak" acid, is *enormously stronger than water,* and we find accordingly that the degree of hydrolysis of a decinormal solution of sodium hydrosulphide in water at 25° is only 0.14 per cent.

It should be noted that substances such as phosphorus tribromide (p. 273), silicon tetrachloride (p. 449) and other compounds of purely non-metallic elements are *completely* hydrolyzed by water. These substances are not salts, and ionic equilibria are not involved in their decomposition.

The Action of Acids on Insoluble Sulphides. — The interaction of sulphides and acids is itself so important a matter in chemistry, and is so similar in theory to many other kinds of actions, that some attention must be given to it here, although the *quantitative* discussion of the various points involved will be more appropriately taken up in a later chapter (pp. 572-578). The common method of preparing hydrogen sulphide from ferrous sulphide (p. 321) affords a suitable illustration.

Since ferrous sulphide is but slightly soluble in water, the action proceeds by a rather complex series of equilibria:

$$FeS(\text{solid}) \leftrightarrows FeS(\text{dslvd}) \leftrightarrows Fe^{++} + S^= \ \big\} \leftrightarrows H_2S(\text{dslvd})$$
$$2HCl \leftrightarrows 2Cl^- + 2H^+ \ \big\} \qquad \rightleftarrows H_2S(\text{gas}).$$
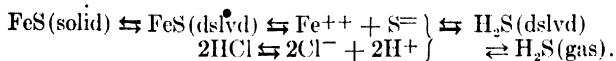
It will be seen that a number of reversible changes are involved, and the question is, why does the reaction proceed forward, as it

does? To answer this question, a consideration of each of the equilibria, separately, is required.

1. The dissolved hydrogen sulphide is very feebly ionized, and maintains a smaller concentration of sulphide-ion $S^=$ than does ferrous sulphide, in spite of the comparative insolubility of the latter. Hence, the $S^=$ formed from the FeS is continuously being removed by union with the hydrogen-ion furnished by the acid, and all the other equilibria are constantly displaced forward on this account. The action is therefore, in essence, like neutralization (p. 258).

2. The extent to which the union of sulphide-ion and hydrogen-ions approaches completeness depends on the magnitude of the *product* of their concentrations (p. 210). Here, although $[S^=]$ is minute, on account of the very low solubility of FeS, $[H^+]$ is large on account of the great dissociation of the HCi and the fact that a concentrated solution of the acid can be used. Thus the *product* is still large enough to carry the reaction forward.

3. The fact that hydrogen sulphide is fairly soluble in water *hinders* the progress of the action. It prevents that free escape of one product which is so constantly a factor in promoting reversible chemical changes. Here the retention of H_2S in the solution makes it impossible, finally, to maintain $[S]^=$ below a certain fixed concentration, dependent upon the particular concentration of hydrogen-ion H^+ present, and since, as the reaction proceeds, the concentration of ferrous-ion Fe^{++} also steadily increases, we are inevitably tending towards a point where the product of the concentrations of $S^=$ and of Fe^{++} will be such that no more FeS will dissolve. Thus, if cadmium sulphide CdS, which is less soluble than ferrous sulphide, is employed along with rather dilute hydrochloric acid, a concentration of hydrogen sulphide sufficient to stop the action accumulates even before the liquid is saturated with the gas.

4. There are then two ways of making this action continuous. Either more concentrated hydrochloric acid, giving a higher concentration of H^+, may be used to force the formation of more H_2S (by union of $2H^+$ and $S^=$), or the reverse action, due to accumulation of H_2S (dissolved), may be diminished mechan-

ically by leading air through the mixture (p. 157) and so removing the hydrogen sulphide as fast as it is formed. Either plan will cause complete interaction with the cadmium sulphide.

5. When a still more insoluble sulphide, like cupric sulphide CuS is employed, a concentration of H^+ sufficient to reduce the concentration of $S^=$ in the solution below the limiting value cannot be obtained *with any acid*. The reaction therefore automatically comes to a stop almost as soon as it begins.

Classification of Insoluble Sulphides. — In analytical chemistry, advantage is taken of the different solubilities of the sulphides, for the purpose of identifying the metallic elements, and of separating mixtures containing several such elements. Three classes are distinguished.

1. The sulphides of silver, copper, mercury, and some other metals are exceedingly insoluble, and, therefore, do not interact with dilute acids as does ferrous sulphide (p. 321). These may therefore be made by leading hydrogen sulphide into solutions of their salts:

$$CuSO_4 + H_2S \leftrightarrows CuS\downarrow + H_2SO_4.$$
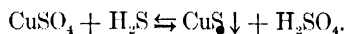
The acid produced has scarcely any effect upon the sulphide, and almost no reverse action is observed. In this action the sulphide-ion is the active substance and, by its removal, all the equilibria are displaced forwards. The precipitation of black PbS from a solution of lead acetate is used as a *test* for hydrogen sulphide.

2. The sulphides of iron, zinc, and certain other metals are insoluble in water, but not so much so as the last class. Hence they are decomposed by dilute acids, and the reverse of the above action takes place almost completely. These sulphides must therefore be made, either by combination of the elements, or by adding a soluble sulphide to a solution of a salt:

$$FeSO_4 + (NH_4)_2S \leftrightarrows FeS\downarrow + (NH_4)_2SO_4.$$
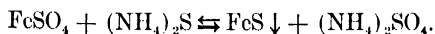
No acid is produced in this sort of interaction, and the very minute solubility of the sulphide of iron or zinc in water renders the change nearly complete.

3. The sulphides of barium, calcium, and some other metals,

although insoluble in water, are hydrolyzed by it, and give soluble products, the hydroxide and hydrosulphide:

$$2CaS + 2H_2O \leftrightarrows Ca(OH)_2 + Ca(SH)_2.$$
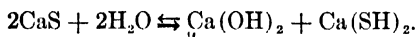
They may be prepared by direct union of the elements, and from the sulphates by reduction with carbon. But they are not precipitated by hydrogen sulphide or ammonium sulphide.

Polysulphides. — When sulphur is shaken with a solution of a soluble sulphide, such as sodium sulphide, it dissolves, and evaporation of the solution leaves residues, varying in composition from Na_2S_2 to Na_2S_5. These appear to be mixtures composed mainly of Na_2S and Na_2S_4.

When an acid is poured into sodium polysulphide solution, minute spherules of rhombic sulphur are precipitated:

$$Na_2S_4 + 2HCl \rightarrow 2NaCl + H_2S \uparrow + 3S \downarrow.$$
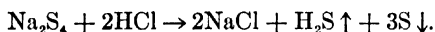
The Chemical Relations of the Element Sulphur. — In combination with metals and hydrogen, sulphur is bivalent, forming compounds like H_2S, FeS, CuS, and HgS. In combination with non-metals, however, the valence is frequently greater, the maximum being seen in sulphur trioxide, where the sulphur is sexivalent. Its oxides are acid-forming, and it is, therefore, a non-metal.

Exercises. — 1. How could the decomposition of hydrogen sulphide at 310° be rendered, (a) more complete, (b) less complete? Would the percentage decomposed be affected, (a) by reducing the pressure, (b) by mixing the gas with an indifferent gas?

2. What are the relative volumes of the gases (p. 189) in the action of, (a) hydrogen iodide and sulphur, (b) hydrogen sulphide and sulphur dioxide?

3. Formulate completely, after the model on p. 256, the actions of (a) hydrogen sulphide and cupric sulphate solution; (b) ammonium sulphide and ferrous sulphate. In each case explain which equilibrium determines the direction of the action.

4. Is heat evolved, or absorbed, when monoclinic sulphur

changes over to rhombic sulphur? Is heat evolved, or absorbed, when S_λ changes over to S_μ? Apply Van't Hoff's Law (p. 216).

. 5. Would equal weights of rhombic and monoclinic sulphur give •out equal or different amounts of heat on burning? If different, which would give more and which less?

6. Why is chlorine an antidote for hydrogen sulphide poisoning (see p. 284)?

7. Why does a solution of sodium sulphide in water tend to deposit sulphur on standing in contact with air?

8. Apply each of the two methods (pp. 301-305) of writing complex equations to balance the following skeleton reactions:

(a) $K_2Cr_2O_7 + HCl + H_2S \rightarrow KCl + CrCl_3 + H_2O + S$.

(b) $KMnO_4 + HCl + H_2S \rightarrow KCl + MnCl_2 + H_2O + S$.
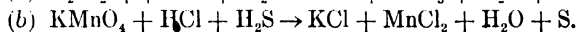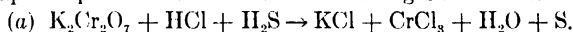
CHAPTER XXIII

OXIDES AND OXYGEN ACIDS OF SULPHUR

THERE are two familiar oxides, namely sulphur dioxide or sulphurous anhydride SO_2, and sulphur trioxide or sulphuric anhydride SO_3. Each of these dissolves in water and combines with it to form an acid. The former gives sulphurous acid H_2O,SO_2 or H_2SO_3, and the latter sulphuric acid H_2O,SO_3 or H_2SO_4.

SULPHUR DIOXIDE AND SULPHUROUS ACID

Preparation of Sulphur Dioxide SO_2. — In *industrial practice* sulphur dioxide *is obtained* in three ways:

1. By burning sulphur (p. 36).
2. By burning natural sulphides, such as pyrite:

Skeleton: $\qquad FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2.$

Balanced: $\qquad 4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2.$

With fairly pure pyrite the combustion has only to be started, the heat evolved in the reaction being sufficient to offset loss of heat by radiation and to keep it going of its own accord. But with some sulphides, like zinc blende ZnS, which is used as a source of sulphur dioxide as well as of zinc, the air must be strongly heated throughout to maintain the combustion:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$
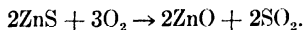
Forced combustion of an ore, like this, is called **roasting, or calcining,** and is the first stage towards obtaining the metal. The oxide is subsequently reduced by heating with coke.

3. By dropping concentrated sulphuric acid into red-hot iron retorts:

$$2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + O_2.$$
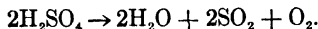
In the laboratory a steady stream of the gas is easily obtained by dropping hydrochloric acid upon crystals of sodium-hydrogen sulphite (Fig. 30, p. 62):

$$NaHSO_3 + HCl \rightleftarrows NaCl + H_2SO_3, \qquad (1)$$
$$H_2SO_3 \rightleftarrows H_2O + SO_2 \uparrow . \qquad (2)$$
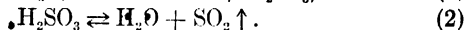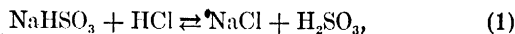
This method takes advantage of two facts: (*a*) that sulphurous acid is only slightly ionized in solution, which renders reaction (1) practically complete, especially in the presence of an *excess* of HCl, an active acid (see p. 244), and (*b*) that sulphurous acid is unstable and decomposes (equation 2) when there is not a large excess of water present.

Sulphur dioxide can also be made by the reduction of concentrated sulphuric acid by copper at a high temperature:

$$2H_2SO_4 + Cu \rightarrow 2H_2O + SO_2 + CuSO_4.$$

Some easily oxidized non-metals, such as carbon and sulphur, act in the same way, $C + 2H_2SO_4 \rightarrow 2H_2O + 2SO_2 + CO_2$.

Physical and Chemical Properties. — Sulphur dioxide is a gas possessing a penetrating and characteristic *odor*. This is frequently spoken of as the "odor of sulphur," but it should be remembered that sulphur itself has scarcely any smell at all. The weight of the G.M.V. of the gas (65.54 g.) shows it to be more than *twice as heavy as air*. By means of a freezing mixture of ice and salt (Fig. 86), the gas is easily condensed in a U-tube to a transparent mobile fluid, which boils at − 8°. At 20°, the liquid

Fig. 86.

gives a vapor pressure of only 3¼ atmospheres, so that the liquid is handled and sold in glass syphons or in sealed tin cans. The *solubility* of the gas in water is very pronounced, about 4000 volumes of the gas dissolving in 100 volumes of water at 20° and 760 mm. The solution is completely freed from the gas by boiling (compare p. 166).

As regards **chemical properties**, sulphur dioxide is **stable** (p. 43).
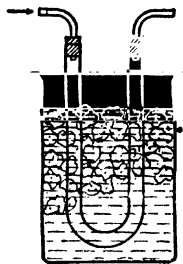
It **unites with water** to form sulphurous acid H_2SO_3, which is unstable, and exists only in solution.

Since the maximum valence of sulphur is 6, sulphur dioxide, in which but four of the valences of sulphur are used, is **unsaturated** (see p. 132). It is therefore still able to combine directly with suitable elements, such as chlorine and oxygen. When it is mixed with chlorine in sunlight, **sulphuryl chloride** SO_2Cl_2 is produced.

Liquefied sulphur dioxide is employed for bleaching straw, wool, and silk (see p. 297).

Enormous quantities of sulphur dioxide are employed in the manufacture of sulphuric acid and of sulphites.

Properties of Sulphurous Acid H_2SO_3. —Sulphurous acid, in aqueous solution, shows all the properties of a *transition acid*. As already noted, concentrated solutions are very unstable. A solution of sulphurous acid therefore smells strongly of sulphur dioxide.

$$SO_2 \text{ (gas)} \rightleftarrows SO_2 \text{ (dslvd)} + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows H^+ + SO_3^=.$$
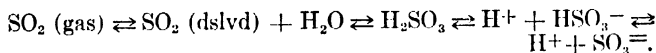
Being rather easily convertible into sulphuric acid H_2SO_4, sulphurous acid is *a reducing agent*. Thus oxygen from the air acts slowly upon the solution:

$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$$

and iodine is turned into hydrogen iodide:

$$H_2SO_3 + H_2O + I_2 \rightarrow H_2SO_4 + 2HI.$$
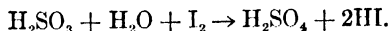
Hydrogen peroxide, potassium permanganate, and other oxidizing agents convert sulphurous acid into sulphuric acid likewise.

Sulphurous acid has the power of **uniting directly** with many organic coloring matters and, since the products of this union are usually colorless, it is employed as a bleaching agent. It is especially useful with chemically reactive materials like silk, wool, and fragile structures like straw, which are likely to be destroyed if bleaching powder is used. The compounds thus formed are unstable, and lose the sulphurous acid again. Hence,

wool yellows with age, and straw hats lose their whiteness. As a disinfectant it acts, perhaps, by addition likewise.

. To prevent the growth of fungi or other organisms, wine casks are fumigated with sulphur dioxide before being filled. Dried peaches and apples are prepared by exposing slices of the fruit on trays to sulphur dioxide. The sulphurous acid produced bleaches the fruit, keeps insects away, and prevents the formation of dark-colored substances during the subsequent drying.

As a **dibasic acid,** sulphurous acid forms **normal salts** like Na_2SO_3, and **acid salts** like $NaHSO_3$.

Sulphites. — The **acid sulphites** (or **bisulphites,** compare p. 347) of the alkali metals, $KHSO_3$ and $NaHSO_3$, when in solution, are acid in reaction. Solutions of the **neutral sulphites,** however, react **alkaline.** Both series of salts are readily decomposed by strong acids to give free sulphurous acid, and the latter partly decomposes, yielding sulphur dioxide (p. 333).

Calcium bisulphite solution, $Ca(HSO_3)_2$, is used to dissolve the lignin out of wood, and leave the pure cellulose (paper pulp) employed in the manufacture of paper (see p. 514).

When **heated,** sulphites undergo decomposition. The sulphates, being the most stable of *all* the salts of sulphur acids, are formed when the salts of *any* of those acids are decomposed by heating. The nature of the particular salt determines what other products shall appear. Thus, with sodium sulphite Na_2SO_3, one molecule of the sulphite furnishes three atoms of oxygen, sufficient to oxidize three other molecules, and leaves one molecule of sodium sulphide behind:

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4.$$
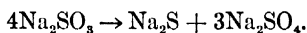
The sulphites are as readily **oxidized** as is the acid itself. They are slowly converted, both in solution and in the solid form, by the influence of the oxygen of the air, into sulphates.

●

SULPHUR TRIOXIDE AND SULPHURIC ACID

Sulphur Trioxide. — Sulphur dioxide and oxygen, when heated together to 400°, unite very slowly with evolution of heat to give sulphur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3 + 45,200 \text{ calories.}$$
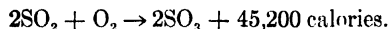
This reaction, however, cannot be utilized for the manufacture of sulphur trioxide except under special conditions, for at 400° the union takes place far too slowly for use in industrial work, while at higher temperatures the reverse action becomes appreciable and poor yields are obtained. If we apply Van't Hoff's law to the reversible reaction: $2SO_2 + O_2 \rightleftarrows 2SO_3$ we see that, since the forward change is *exothermic*, raising the temperature will favor the backward change. In actual practice it is found that at 400°, 98–99 per cent of the materials unite; at 700°, only 60 per cent; at 900°, practically none.

Sulphur trioxide is a white solid which exists in two allotropic crystalline forms. One melts at 15°, and is therefore fluid at ordinary temperatures. The other vaporizes without melting at 50°. Both forms react vigorously with water, causing a hissing noise due to the steam produced by the heat of the union:

$$SO_3 + H_2O \rightarrow H_2SO_4.$$
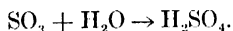
Sulphur trioxide combines also with sulphuric acid to give **oleum**, or *fuming sulphuric acid*, $H_2S_2O_7$:

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7.$$
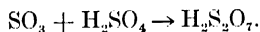
The Contact Process for Sulphuric Acid. — The interaction of sulphur dioxide and oxygen is hastened by many substances, such as glass, porcelain, ferric oxide and, more especially, finely divided platinum, which remain themselves unchanged and simply act as contact or catalytic agents. The *contact process*, as this is called, is now very extensively used in the manufacture of sulphuric acid.

The efficiency of the contact agent depends on the amount of surface it presents to the gases. The action may be illustrated by dipping asbestos in a solution of chloroplatinic acid and then heating the mineral in the Bunsen flame:

$$H_2PtCl_6 \rightarrow Pt + 2HCl \uparrow + 2Cl_2 \uparrow.$$
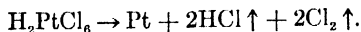
The platinum is thus spread in a fine grey powder on the fibers of the asbestos. The latter is placed in a tube (Fig. 60, p. 176),
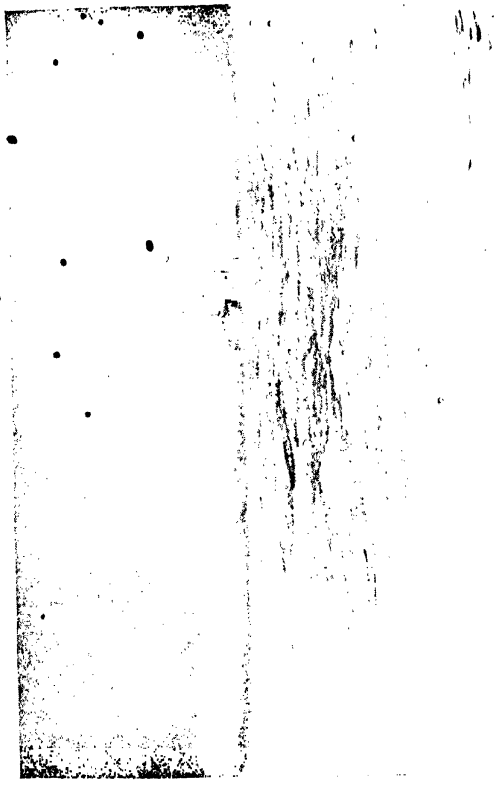
CHEMICAL SMOKE-SCREENS AGAINST SUBMARINES
A VESSEL USING OLEUM

where a mixture of oxygen (or air) and sulphur dioxide may be passed over the heated material. The sulphur trioxide issues as vapor at the other end of the tube, where its presence is recognized by the dense fumes (droplets of sulphuric acid), produced when it meets the moisture in the air. The vapor can be condensed to liquid form in a cooled flask.

In practice the contact agent employed is *platinum*, dispersed in a very finely-divided condition throughout a suitable carrying material, or *base*. The Grillo process uses, as a base *magnesium sulphate*. This gives a catalytic mass just as active as platinized asbestos, and requires only one-hundredth part the amount of platinum. With *silica gel* (p. 452) as a base, the platinum content of the contact mass can be still further reduced. This is a very important point in the economics of the process.

It is absolutely necessary, in employing the contact process, to remove from the sulphur dioxide all traces of substances such as arsenious oxide and similar impurities derived from the calcining of pyrite or some other mineral sulphide. The most minute quantities of these substances act as *poisons* on the catalytic agent, and soon render it quite inoperative. The sulphur dioxide is therefore very carefully purified before reaching the contact chamber. *Excess oxygen* is used in the reacting mixture, in order to drive the reaction more readily towards complete formation of SO_3 (compare p. 209). The temperature in the contact chamber is kept between 380° and 450°. The system has a tendency to get hotter during the reaction, owing to the heat evolved. This tendency, if unchecked, would lead to a decreased yield of sulphur trioxide; the cold entering gases are therefore first led over the outside of the pipes which contain the catalyst, in order to keep the temperature constant inside.

The issuing gases, consisting mainly of sulphur trioxide vapor mixed with excess oxygen, are condensed by being led into 97–99 per cent sulphuric acid, the concentration of the liquid being maintained at this point by a regulated influx of water. If oleum, or fuming sulphuric acid, is required, the addition of water is omitted.

It would seem to be simpler to dissolve the gaseous sulphur trioxide in water. to give sulphuric acid $H_2O + SO_3 \rightarrow H_2SO_4$,

rather than in 98 per cent sulphuric acid, but this cannot be done. The mixture $O_2 + SO_3$ is very incompletely absorbed by water. When a bubble of this mixture enters water, the latter evaporates into the bubble in the attempt to saturate the space occupied by the bubble with water vapor (p. 73). The water which so evaporates, however, combines immediately with the sulphur trioxide to form a fog, consisting of droplets of liquid sulphuric acid, and so more and more water evaporates into the bubbles. Now the molecules of SO_3, so long as they remain gaseous, move with great velocity, namely 292 meters per second at room temperature, and still faster in this hot gaseous mixture (see p. 54). Hence, all the molecules that escape combination with the water vapor, strike the wall of the bubble, and combine with the water in a few seconds. The droplets of sulphuric acid, forming the fog, however, are not molecules but large aggregates of molecules. They do not therefore move like the molecules of a gas, but are relatively stationary. The chance of their striking the wall of the bubble is therefore reduced enormously. Hence, after the sulphur trioxide that escapes combination has dissolved, the droplets of fog, carried by the excess of oxygen, can be bubbled through a whole series of vessels of water in succession without any significant amount of the droplets being dissolved. The same fog can be shaken in a flask with water, violently and continuously, without any appreciable solution. When the water is thrown, by the shaking, through the oxygen, the oxygen is split up by the water, and driven about, but the fog particles move with the oxygen, so that the water never reaches them. On the other hand, when the mixture of gases bubbles through 97–99 per cent sulphuric acid, as is done in practice, there is practically no water available for evaporation, the sulphur trioxide remains gaseous, and its rapidly moving molecules in a few seconds have all plunged into the sulphuric acid and combined with it, either uniting with the 1 to 3 per cent of water present or, when oleum is made, uniting with the sulphuric acid to form $H_2S_2O_7$.

This case affords an admirable illustration of the importance of physics in practical chemistry (p. 25). The chemical reaction occurs with water, but the physical condition of the fog of sulphuric acid prevents its dissolving and, if water were used in a

factory, a large proportion of the sulphuric acid would pass with the excess of oxygen into the air and be lost. In fact, it would kill vegetation, and make life unbearable in the neighborhood.

Chamber Process for Sulphuric Acid. — Although salts of sulphuric acid, such as calcium sulphate $CaSO_4$, are exceedingly plentiful in nature, the preparation of the acid by chemical action upon the salts is not practicable. The sulphates, indeed, interact with all acids, but the actions are reversible. The completion of the action by the plan used in making hydrogen chloride (p. 162), involving the removal of the sulphuric acid by distillation, would be difficult on account of the involatility of this acid. It boils at $330°$; and suitable acids, less volatile still, which might be used to liberate it, do not exist. We are therefore compelled to build up sulphuric acid from its elements.

The gases, the interactions of which result in the formation of sulphuric acid, are: water vapor, sulphur dioxide, nitrous anhydride N_2O_3,* (see p. 399), and oxygen. These are obtained, the first by injection of steam, the second usually by the burning of pyrite, the third from nitric acid HNO_3 (see below, p. 341), and the fourth by the introduction of air. The gases are thoroughly mixed in large leaden chambers, and the sulphuric acid forms droplets which fall to the floors. In spite of elaborate investigations, instigated by the extensive scale upon which the manufacture is carried on and the immense financial interests involved, some uncertainty still exists in regard to the precise nature of the chemical changes which take place. According to Lunge, supporting the view first suggested by Berzelius, the greater part of the product is formed by two successive actions, the first of which yields a complex compound that is decomposed by excess of water in the second:

$$H_2O + 2SO_2 + N_2O_3 + O_2 \rightarrow 2SO_2 \begin{matrix} \diagup O - H \\ \diagdown O - NO \end{matrix} \tag{1}$$
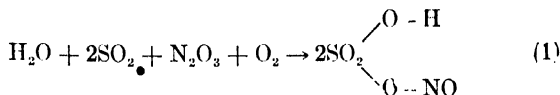
* This gas is unstable, breaking up in part into nitric oxide NO and nitrogen tetroxide NO_2: $N_2O_3 \rightleftarrows NO + NO_2$. In this process, however, the mixture behaves as if it were all N_2O_3, and so only nitrous anhydride is named in this connection.

The group – NO, nitrosyl, is found in many compounds. **Here,** if it were displaced by hydrogen, sulphuric acid would result. Hence this compound is called **nitrosylsulphuric acid:**

$$2SO_2\begin{matrix}O-H\\\\O-NO\end{matrix} + H_2O \rightleftarrows 2SO_2\begin{matrix}OH\\\\OH\end{matrix} + N_2O_3. \quad (2)$$
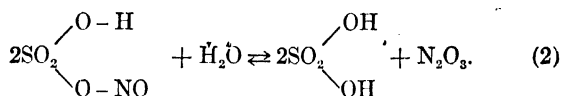
‑The equations (1) and (2) are not partial equations for one interaction, but represent distinct actions which can be carried out "separately. In a properly operating plant, indeed, the nitrosylsulphuric acid is not observed. But when the supply of water is deficient, white "chamber crystals," consisting of this substance, collect on the walls.

The explanation of the success of this seemingly roundabout method of getting sulphuric acid is as follows: The direct union of sulphur dioxide and water to form sulphurous acid is rapid, but the action of free oxygen upon the latter, $2H_2SO_3 + O_2 \rightarrow 2H_2SO_4$, is exceedingly slow. Reaching sulphuric acid by the use of these two changes, although they constitute a direct route to the result, is not feasible in practice. On the other hand, both of the above actions, (1) and (2), happen to be much more speedy, and so, by their use, more rapid production of the desired substance is secured at the expense of a slight complexity.

The progress of the first action is marked by the disappearance of the brown nitrous anhydride and, on the introduction of water, the completion of the second stage results in the reproduction of the same substance. The nitrous anhydride takes part a large number of times in these changes, and so facilitates the conversion of a great amount of sulphur dioxide, oxygen, and water into sulphuric acid, without much diminution of its quantity. Some is unavoidably lost, however.

This loss of nitrous anhydride is made good by the introduction of nitric acid vapor into the chamber. This acid is made from concentrated sulphuric acid and commercial sodium nitrate $NaNO_3$:

$$NaNO_3 + H_2SO_4 \rightleftarrows HNO_3 \uparrow + NaHSO_4.$$
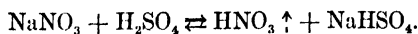
On account of the volatility of the nitric acid, a moderate heat is sufficient to remove it from admixture with the other substances, and its vapor is swept along with the other gases into the apparatus. The first reaction which this vapor undergoes may be written:

$$H_2O + 2SO_2 + 2HNO_3 \rightarrow 2H_2SO_4 + N_2O_3.$$
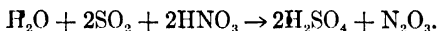
The N_2O_3 formed is now immediately available to take part in the successive cycles of reactions already discussed.

Relative Speed of Consecutive Reactions. — In consecutive reactions, as we have already mentioned (p. 313), the second uses materials produced by the first. It may be noted that if the second action is as speedy as the first, or speedier, then no intermediate products will be detectable. This is the case with the chamber process reactions, when sufficient steam is introduced, for under these circumstances no solid nitrosylsulphuric acid is deposited. If the second reaction is slower than the first, then the products of the first reaction will accumulate, and become noticeable.

The conception of consecutive reactions enables us to understand and remember some significant facts. For example, it was mentioned that when dry sulphur is oxidized, we obtain sulphur dioxide, but when moist sulphur is oxidized, by the air or otherwise, the only product is sulphuric acid (p. 320). This change may be conceived of as proceeding in two stages:

$$S + O_2 + H_2O \rightarrow H_2SO_3,$$
$$2H_2SO_3 + O_2 \rightarrow 2H_2SO_4,$$
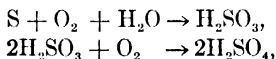
which would be consecutive reactions. Since oxidation of solid sulphur can proceed only on the surface, it is slow. Since the sulphurous acid is dissolved, and every molecule of it is accessible to the dissolved oxygen, or oxidizing agent, the second action should be speedier and consume the product of the first action as fast as it is formed. It is, therefore, quite natural that no sulphurous acid should be detectable when water is present.

Details of the Chamber Process. — The sulphur dioxide is produced in a row of furnaces A (Fig. 87). The gases from the various furnaces pass into one long dust-flue, in which they are mingled with the proper proportion of air, and deposit oxides of iron and of arsenic, and other materials which they transport mechanically. From this flue they enter 'the Glover tower G, in which they acquire the oxides of nitrogen. Having secured all the necessary constituents, excepting water, the gases next
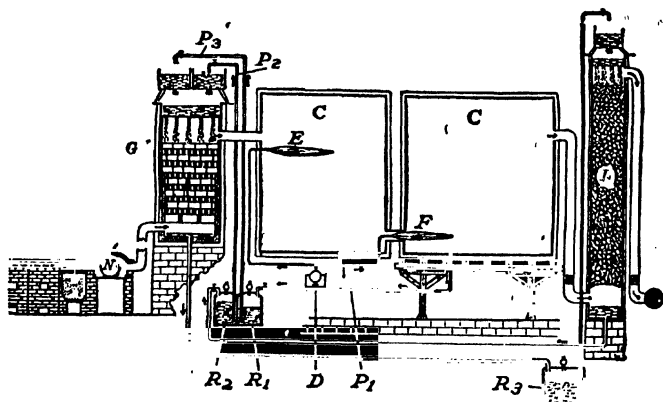
Fig. 87.

enter the first of the lead chambers C, large structures lined completely with sheet lead. These measure as much as $100 \times 40 \times 40$ feet, and have a total capacity of 150,000 to 200,000 cubic feet. As the gases drift through these chambers they are thoroughly mixed, and an amount of steam considerably in excess of that actually required is generated in a boiler D and injected into the chambers at various points E and F. The sulphuric acid formed, along with the excess of steam, condenses and collects upon the floor of the chamber, whence it is run through a pipe P_1 into a reservoir R_1, while the unused gases, chiefly nitrous anhydride and nitrogen, the latter derived from the air originally admitted, find an exit into the Gay-Lussac tower L.

This is a tower about fifty feet in height, filled with tiles, over which *concentrated* sulphuric acid continually trickles. The

object of this tower, to catch the nitrous anhydride and enable it to be reëmployed in the process, is accomplished by a reversal of action (2) on p. 340. The acid which accumulates in the vessel at the bottom of this tower contains, therefore, nitrosylsulphuric acid, and by means of compressed air this acid is forced from a reservoir R_2 through a pipe P_2 up to a vessel at the top of the Glover tower G. A neighboring vessel at the top of this tower is filled with dilute sulphuric acid, forced up by compressed air from the reservoir R_1 through a pipe P_3 as required, and when the contents of both vessels are mixed by allowing their contents to trickle down through the tower, nitrous anhydride is once more set free by the interaction of the water in the dilute acid (action (2)). The Glover tower is filled with broken flint or tiles, in order that the descending liquid may offer a large surface to the hot gases ascending the tower, and thereby facilitate the acquisition by these gases of a sufficient quantity of nitrous anhydride. Their high temperature also causes a considerable concentration of the diluted sulphuric acid as it trickles downward. This concentrated acid, after traversing this tower, is run into a reservoir R_3, whence as much as is needed is forced by compressed air to the top of the Gay-Lussac tower L to be used once more for the absorption of nitrous anhydride.

To replace the part of the nitrous anhydride which is inevitably lost, fresh nitric acid is furnished by small open vessels N, containing sodium nitrate and sulphuric acid, placed in the flues of the pyrite-burners. About 4 kg. of the nitrate are consumed for every 100 kg. of sulphur.

Concentration of "Chamber Sulphuric Acid." — The acid which drains from the chambers into the reservoir R_1 ("chamber acid") contains but 60 to 70 per cent of sulphuric acid, and has a specific gravity of 1.5–1.62.

This crude sulphuric acid is applicable directly in some chemical manufactures, such as the preparation of superphosphates (p. 527). For many purposes, however, a more concentrated acid is required. (Some is available, of course, from the more concentrated product accumulating in the reservoir R_3). Concentration of the chamber acid is effected by heating, to evapo-

rate off water, in pans lined with lead, which are frequently placed over the pyrite-burners in order to economize fuel. The evaporation in lead is carried on until a specific gravity 1.7, corresponding to 77 per cent concentration, is reached. Up to this point the sulphate of lead formed by the action of the sulphuric acid produces a crust which protects the metal from further action. When a still more concentrated acid is wanted other methods of driving off the water, such as the cascade system or the Gaillard tower, must be employed.

The **cascade system** consists of a series of small silica or silicon-iron basins set over an inclined flue, and so placed that each basin delivers by a spout into the one below. The flue is heated by gas or coke firing at the lower end, and dilute acid is fed continuously into the basin at the top end. As the acid passes from basin to basin, it meets hotter and hotter conditions and becomes more and more concentrated.

The **Gaillard plant** consists essentially of a large hollow tower built of acid-resisting stone, and filled with small fragments of similar material. Dilute acid is sprayed in at the top, and meets hot furnace gases injected in at the bottom. Most of the water contained in the acid is carried off by these gases, and concentrated acid collects at the bottom of the tower.

A more convenient method of obtaining very concentrated acid, which avoids the difficulties of evaporation entirely, is to add to the chamber acid the requisite quantity of **oleum,** prepared by the contact process already described. Commercial sulphuric acid, **oil of vitriol,** has a specific gravity 1.83–1.84, and contains about 93.5 per cent H_2SO_4.

Commercial sulphuric acid is always **impure.** It contains, for example, lead sulphate, which appears as a precipitate when the acid is diluted, as well as arsenic trioxide and oxides of nitrogen in combination.

Physical Properties. — Pure hydrogen sulphate (100% sulphuric acid H_2SO_4) has a sp. gr. 1.85 at 15°. When cooled, it crystallizes (m.-p. 10.5°). At 150°–180° the acid begins to fume, giving off sulphur trioxide. It boils at 330°, but loses more sulphur trioxide than water and finally yields an acid of constant

boiling-point (338°) and constant composition (98.33 per cent). The vapor is largely decomposed into free water and sulphur trioxide, which recombine when it condenses.

Hydrogen sulphate mixes with water in all proportions, with considerable evolution of heat (see p. 218). Its solution (sulphuric acid) is thus much more 'stable (*i.e.*, it contains much less energy)' than the pure substance, and hence the latter absorbs water greedily.

• **Chemical Properties of Hydrogen Sulphate.** — 1. The compound is **not** exceedingly **stable**, for dissociation into water and sulphur trioxide, as noted above, begins far below the boiling-point. In the state of vapor it is practically completely dissociated at 416°, as is shown by the density of the vapor. When raised suddenly to a red heat it is broken up completely into water, sulphur dioxide, and oxygen (see p. 332).

2. Hydrogen sulphate combines vigorously with water to form several isolable hydrates, of which the most important is the **monohydrate**, $H_2SO_4.H_2O$ (m.-p. 10°). On this account, very concentrated sulphuric acid is able to take the elements of water from compounds containing hydrogen and oxygen, especially those containing these elements in the proportion 2H : 1O (see p. 517). Thus paper, which is largely cellulose $(C_6H_{10}O_5)_x$, wood (which contains much cellulose) and sugar $C_{12}H_{22}O_{11}$ are charred by it, and carbon is set free:

$$C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O.$$
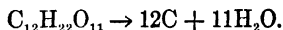
For the same reason, concentrated sulphuric acid is used in drying gases with which it does not interact. It is the most common **dehydrating agent** used in chemistry.

3. On account of the large quantity of oxygen which hydrogen sulphate contains, and its instability when heated, it also behaves as an **oxidizing agent**. This property has already been illustrated in connection with the action of the acid upon carbon, sulphur, and copper (p. 333), hydrogen iodide (p. 278), and hydrogen bromide (p. 273). The hydrogen sulphate is in consequence reduced to sulphur dioxide, and even to free sulphur or hydrogen sulphide. The metals, from the most active down to

silver (p. 240), are capable of reducing it at moderately high temperatures, the sulphates * being formed. The more active metals, like zinc, reduce it to hydrogen sulphide, the less active, like copper, give sulphur dioxide. Gold and platinum alone do not interact with it. Free hydrogen itself is oxidized to water when passed into hydrogen sulphate at '160°:$H_2SO_4 + H_2 \rightarrow SO_2 + 2H_2O$.

∽ **Chemical Properties of Aqueous Hydrogen Sulphate.** — 1. Except in concentrated solutions (normal or above) the oxidizing effects of the undissociated, molecular substance are not encountered. Ionization takes place in two stages:

$$H_2SO_4 \rightleftarrows H^+ + HSO_4^- \rightleftarrows H^+ + SO_4^=.$$

2. In aqueous solution, sulphuric acid is much more active as *an acid* than is sulphurous acid, but is somewhat inferior in this respect to hydrochloric acid HCl and nitric acid HNO_3. Like other active, soluble acids, its solution turns litmus red, gives hydrogen upon addition of active metals, and enters into double decomposition with bases and salts. Thus, insoluble barium sulphate is obtained as a white precipitate by the action of dilute sulphuric acid on any soluble barium salt:

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 \downarrow + 2HCl.$$
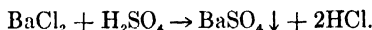
Any soluble sulphate will, of course, give the same precipitate with barium chloride, and the action is used as a **test** for this ion. Some other salts of barium are also insoluble in water, but the sulphate is recognized by the fact that it is too insoluble to be acted upon by dilute pure hydrochloric acid or nitric acid. The other insoluble salts of barium interact with these acids and dissolve. The addition of one of these acids is therefore part of the **test** for $SO_4^=$ ion.

3. On account of its high boiling-point, the double decompositions of the concentrated acid can be *used for preparing more volatile acids:*

* Note that the sulphates, and *not* the oxides of the metals are produced. Oxides of metals could not be *formed in* concentrated sulphuric acid, because they interact with the latter much more vigorously than do the metals, to give the sulphates (compare p. 167).

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl \uparrow \text{ (gas at room temp.).}$$
$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3 \uparrow \text{ (volatile at } 86°\text{).}$$
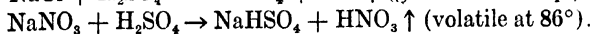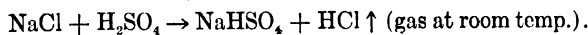
4. Since hydrogen sulphate is dibasic (p. 246), it forms both acid and normal salts, such as $NaHSO_4$ and Na_2SO_4. The acid sulphates are called also bisulphates, because they contain twice as large a proportion of SO_4 to Na, and require twice as much sulphuric acid for their preparation as do the neutral sulphates.

Sulphates. — The **acid sulphates** may be produced either by adding to dilute sulphuric acid half an equivalent of a base, and evaporating: $NaOH + H_2SO_4 \rightarrow H_2O + NaHSO_4$, or by actions in which another acid is displaced, as in making hydrogen chloride (p. 162). These salts are acid in reaction, as well as in name.

When acid sulphates, such as $NaHSO_4$, are heated, water is given off and a *pyrosulphate* (Greek prefix, *fire*) remains.

$$2NaHSO_4 \rightarrow Na_2S_2O_7 + H_2O.$$
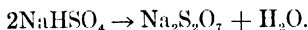
The pyrosulphates are salts of oleum, or fuming sulphuric acid, which has already been mentioned. Oleum possess all of the dehydrating and oxidizing powers of sulphuric acid in an accentuated form, and is widely used in the industries on account of these properties.

The **normal** (or neutral) **sulphates** are obtained by complete neutralization and evaporation, or by the second of the above methods when a sufficient amount of the salt and a higher temperature are used:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl \uparrow .$$
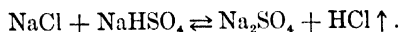
They may also be made by precipitation, by oxidation of a sulphide at a high temperature, $PbS + 2O_2 \rightarrow PbSO_4$, or by addition of sulphur trioxide to the oxide of a metal.

Normal sulphates of the heavy metals decompose at a red heat, some giving off sulphur trioxide, others sulphur dioxide and oxygen. The sulphates of the more active metals and of lead, however, are not affected by heating.

Uses of Sulphuric Acid. — The acid has innumerable applications, some of which will be taken up in detail in later chapters.

It is employed in almost every chemical industry, approximately 6,000,000 tons being produced yearly in the United States alone. It is used in the manufacture of sulphates, hydrochloric acid, nitric acid, sodium carbonate, etc., in refining petroleum, in making fertilizers and dyes, in bleaching, electroplating and so on. Its dehydrating power is especially valuable in making explosives (pp. 596-598).

OTHER ACIDS OF SULPHUR.

Next in importance to sulphurous and sulphuric acids come thiosulphuric acid and persulphuric acid. The compositions of the acids show their relationships:

Hyposulphur*ous* acid,	$H_2S_2O_4$.	Sodium hyposulph*ite*,	$Na_2S_2O_4$.
Sulphur*ous* acid,	H_2SO_3.	Sodium sulph*ite*,	Na_2SO_3.
Sulphur*ic* acid,	H_2SO_4.	Sodium sulph*ate*,	Na_2SO_4.
Thiosulphur*ic* acid,	$H_2S_2O_3$.	Sodium thiosulph*ate*,	$Na_2S_2O_3$.
Persulphur*ic* acid,	$H_2S_2O_8$.	Sodium persulph*ate*,	$Na_2S_2O_8$.

Thiosulphuric acid (Gk. θεῖον, sulphur) is so named because it contains one unit of sulphur in place of one of the units of oxygen of sulphuric acid. Besides the above we have also a series of polythionic acids, namely: dithionic acid $H_2S_2O_6$, trithionic acid $H_2S_3O_6$, tetrathionic acid $H_2S_4O_6$, and pentathionic acid $H_2S_5O_6$.

Thiosulphuric Acid $H_2S_2O_3$. — This acid is not known in the free condition, but its salts are in common use in the laboratory and commercially. Sodium thiosulphate, for example, is prepared by boiling a solution of sodium sulphite with free sulphur. The action resembles the addition of oxygen to sulphurous acid:

$$Na_2SO_3 + S \rightarrow Na_2S_2O_3 \quad \text{or} \quad SO_3^= + S \rightarrow S_2O_3^=.$$
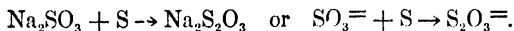
Sodium thiosulphate (popularly, but incorrectly, named "hypo") is used in "fixing" photographs.

By the addition of acids to a solution of sodium thiosulphate, the thiosulphuric acid is set free, but the latter instantly decomposes, giving a precipitate of sulphur:

$$Na_2S_2O_3 + 2HCl \rightleftarrows H_2S_2O_3 + 2NaCl,$$
$$H_2S_2O_3 \rightleftarrows S \downarrow + H_2SO_3 \rightleftarrows H_2O + SO_2 \uparrow.$$
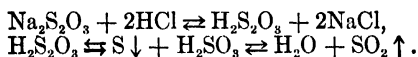
Persulphuric Acid $H_2S_2O_8$. — This, like the other acids just mentioned, is unstable, and can be kept only in dilute solution. Its salts, however, are coming into use for commercial purposes and for "reducing" negatives in photography. The salts are prepared by electrolyzing sodium-hydrogen sulphate $NaHSO_4$ in concentrated solution (Hugh Marshall). The persulphuric acid, formed by the union of the negative ions in pairs as they are discharged on the anode,

$$2HSO_4^- \rightarrow H_2S_2O_8 + 2\ominus,$$
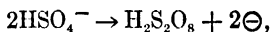
undergoes double decomposition with the excess of sodium bisulphate, and the less soluble sodium persulphate crystallizes out. The other salts are made by double decomposition from this one.

Compounds of Sulphur and Chlorine. — When chlorine gas is passed over heated sulphur, it is absorbed and **sulphur monochloride**, a reddish-yellow liquid, boiling at 138°, is obtained. The molecular weight of this substance, as shown by the density of its vapor, indicates that it possesses the formula S_2Cl_2. When thrown into water, it is rapidly hydrolyzed, producing sulphur dioxide and sulphur: $2S_2Cl_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S$.

Sulphur itself dissolves very freely in the monochloride, and the solution is employed in vulcanizing rubber.

Sulphur dioxide and chlorine gases, when exposed to direct sunlight, unite to form a liquid known as **sulphuryl chloride** SO_2Cl_2. Camphor causes the union to take place much more rapidly, owing to some catalytic effect. The compound is a colorless liquid, boiling at 69°. With water it gives sulphuric acid and hydrogen chloride:

$$SO_2Cl_2 + 2H_2O \rightarrow SO_2(OH)_2 + 2HCl.$$
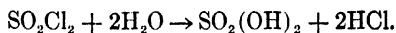
Graphic Formula of Sulphuric Acid. — The actions just mentioned give a clue to the constitution of sulphuric acid. Since chlorine does not combine directly with oxygen, but does combine readily with sulphur, we may assume that, in the formation

of sulphuryl chloride, $SO_2 + Cl_2 \rightarrow SO_2Cl_2$, the chlorine unites more intimately with the sulphur in the molecule SO_2:

$$
\begin{array}{c}
O \diagdown \\
\diagup S + Cl_2 \rightarrow \\
O \diagup
\end{array}
\qquad
\begin{array}{c}
O \diagdown \diagup Cl \\
S \\
O \diagup \diagdown Cl
\end{array}
$$
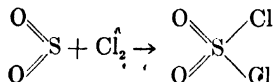
The action of water upon the product is presumably similar to that of water on phosphorus tribromide (p. 273):

$$
\begin{array}{c}
O \diagdown \diagup Cl \quad H - O - H \\
S \\
O \diagup \diagdown Cl \quad H - O - H
\end{array}
\rightarrow 2HCl +
\begin{array}{c}
O \diagdown \diagup O - H \\
S \\
O \diagup \diagdown O - H
\end{array}
$$
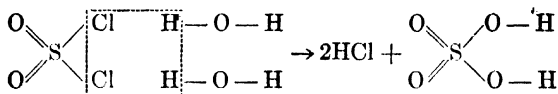
The last is called the **structural formula** of sulphuric acid. It is not thereby implied that the atoms in its molecules are attached precisely in this manner, however, but rather that the *chemical behavior* of the substance, as being partly an oxide and partly an hydroxide of sulphur, is symbolized in this fashion. Such **graphic formulæ** are of great value in expressing the chemical behavior of the complex compounds of carbon.

Exercises. — 1. What ground is there for assigning the formula SO_2 instead of S_2O_4 to sulphur dioxide (p. 333)?

2. Explain why nitric acid is completely displaced by the action of sulphuric acid on sodium nitrate (p. 340).

3. What are the relative volumes, (*a*) of sulphur dioxide and nitrogen (p. 10) resulting from the roasting of pyrite (p. 332), (*b*) of air and sulphur dioxide in making sulphuric acid, (*c*) of nitrogen (left) to sulphur dioxide (used) in making sulphuric acid, when pyrite is the source?

4. Give two reasons why boiling sulphuric acid, when spilt upon the flesh, causes most serious burns.

5. Why is it not desirable to make chamber sulphuric acid of a concentration higher than 60–70 per cent?

6. Justify the nomenclature in the case of hyposulphurous and persulphuric acids.

7. Given normal solutions of sodium hydroxide and sulphuric acid, how would you proceed to form: (*a*) sodium sulphate, (*b*) sodium bisulphate.

8. Explain, by means of ionic equations, why a solution of sodium bisulphite shows an acid reaction, and why a solution of sodium sulphite shows an alkaline reaction.

9. Employ each of the two methods described on pp. 301-305 to balance the following skeleton equations:

(a) $H_2SO_4 + Cu \rightarrow H_2O + SO_2 + CuSO_4$.

(b) $H_2SO_4 + Zn \rightarrow H_2O + H_2S + ZnSO_4$.
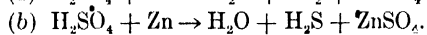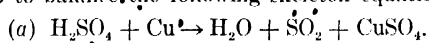
CHAPTER XXIV

SELENIUM AND TELLURIUM. THE PERIODIC SYSTEM

In an earlier chapter (p. 283) we saw that the elements fluorine, chlorine, bromine and iodine exhibited striking similar ities in their chemical properties, and we grouped these four elements together under the name of the halogen family. Now there are two rather rare elements, *selenium* and *tellurium*, which resemble sulphur very markedly in their chemical properties.

Occurrence and Properties of Selenium Se. — Selenium (Greek, *the moon*) occurs free in some specimens of native sulphur, and in combination often takes the place of a small part of the sulphur in pyrite (FeS_2). It is found free in the dust-flues of the pyrite-burners of sulphuric acid works. The familiar forms are, the red precipitated variety, which is amorphous and soluble in carbon disulphide, and the lead-gray, semi-metallic variety, obtained by slow cooling of melted selenium, which is insoluble, and melts at 217°. In the latter form it has some capacity for conducting electricity, which is greatly increased by exposure to light in proportion to the intensity of the illumination. A photometer, using this property, has been devised by Joel Stebbins (1914), for measuring the relative intensity of the light of different stars. Selenium boils at 680°, and at high temperatures has a vapor density corresponding to the formula Se_2.

The element combines directly with many metals, burns in oxygen to form selenium dioxide, and unites vigorously with chlorine.

Compounds of Selenium. — Ferrous selenide, made by heating iron filings with selenium (compare p. 18), when treated with concentrated hydrochloric acid gives hydrogen selenide:

$$FeSe + 2HCl \leftrightarrows H_2Se \uparrow + FeCl_2.$$

352
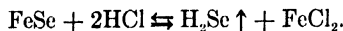
The compound is a poisonous gas, which possesses an odor recalling rotten horse-radish, and is soluble in water. The solution is faintly acid in reaction, and deposits selenium when exposed to the action of the air (compare p. 323). Other selenides, which, with the exception of those of potassium and sodium, are insoluble in water, may be precipitated by leading the gas into solutions of soluble salts of appropriate metals (compare p. 329).

The **dioxide** SeO_2 is a solid substance, formed by burning Se. **Selenious** acid H_2SeO_3 may be made by dissolving the dioxide in hot water, or by oxidizing selenium with boiling nitric acid. Unlike sulphur (p. 320), the element gives little of the higher acid H_2SeO_4 by this treatment. The acid is reduced by sulphurous acid to selenium: $H_2SeO_3 + 2H_2SO_3 \rightarrow 2H_2SO_4 + H_2O + Se.$

No **trioxide** is known. **Selenic acid** H_2SeO_4, a white solid, is made in solution by oxidizing silver selenite with bromine-water:

$$Br_2 + H_2O + Ag_2SeO_3 \rightarrow 2AgBr \downarrow + H_2SeO_4.$$
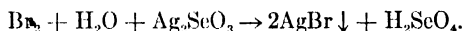
It is much more powerful than sulphuric acid as an oxidizing agent and, even in dilute solution, liberates chlorine from hydrochloric acid: $H_2SeO_4 + 2HCl \rightarrow H_2SeO_3 + H_2O + Cl_2.$

Selenium oxychloride $SeOCl_2$ is a very interesting compound, readily formed by the partial hydrolysis of the **tetrachloride** $SeCl_4$:

$$SeCl_4 + H_2O \rightarrow SeOCl_2 + 2HCl.$$
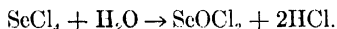
It is a highly corrosive and remarkably active liquid (Lenher).

Tellurium. Te. — Tellurium (Latin, *the earth*) occurs in sylvanite in combination with gold and silver. It is a white, metallic, crystalline substance, melting at 452° (b.-p. 1400°). The free element unites with metals directly, and burns in air to form the dioxide.

The compounds of tellurium are similar in composition and mode of preparation to those of selenium. Some differences in chemical behavior are significant, however. Thus, **tellurious acid** H_2TeO_3 is a very feeble acid and is also somewhat basic, a sulphate $(2TeO_2,SO_3)$ and a nitrate $(Te_2O_3(OH)NO_3)$ being known. In this respect it differs markedly from sulphurous acid. **Telluric acid** does not affect indicators, and is therefore actually

more feebly acidic than is hydrogen sulphide. **Tellurium tetra-chloride** $TeCl_4$, although hydrolyzed by water, exists in solution with excess of hydrogen chloride: $TeCl_4 + 3H_2O \rightleftarrows H_2TeO_3 + 4HCl$, showing the tellurious, acid to be basic in properties and the element tellurium to be, to a certain degree, a metallic element.

The Chemical Relations of the Sulphur Family. — It will be seen that sulphur, selenium, and tellurium are bivalent elements when combined with hydrogen or metals. In combination with oxygen they form unsaturated compounds of the form $X^{IV}O_2$, while their highest valence is found in SO_3, TeO_3, and H_2SeO_4, where they must be sexivalent. The general behavior of corresponding compounds is very similar. At the same time, there is in all cases a progressive change as we proceed from sulphur through selenium to tellurium. The elementary substances themselves, for example, become more like metals, physically, and they show higher and higher melting-points. The affinity for hydrogen decreases, as is shown by the increasing ease with which the compounds H_2X are oxidized in air. The affinity for oxygen likewise decreases, for the elements become increasingly difficult to raise to the highest state of oxidation. On the other hand, the tendency to form higher chlorides becomes greater. We note also that the compounds H_2XO_4 become less and less active as acids, and that a basic tendency begins to assert itself.

Furthermore, just as we have in the halogen family a first member with rather irregular habits, *fluorine*, so we note in the sulphur family a corresponding light element showing decided peculiarities, *oxygen*. Oxygen forms a compound with hydrogen H_2O, which is akin to H_2S in being a weak acid and, as might be predicted, is much more stable. The metallic oxides are very similar in their properties to the metallic sulphides. Ozone may be regarded as oxygen dioxide OO_2, analogous to sulphur dioxide SO_2. The family resemblance in other compounds, however, is more difficult to trace.

The question naturally arises: can we group *all* of the elements into families like the halogen family and the sulphur family? If so, then we shall lighten considerably the burden

of chemical facts that we need to remember, for the behavior of one element in a family will suggest to us immediately how the other members of the same group will act under similar conditions. Classification of this kind is part of the method of science, and furnishes a very useful guide in investigation.

Metallic and Non-Metallic Elements. — Thus far we have found the division into metallic and non-metallic elements very serviceable for classification in terms of chemical relations. **The metallic or positive elements** (p. 240) form positive radicals and ions containing no other element (see p. 222). Thus the metals give sulphates, nitrates, carbonates, and other salts, which furnish a metallic ion, such as Na^+ or K^+, together with the ions $SO_4^=$, NO_3^-, and $CO_3^=$. Their hydroxides, KOH, $Ca(OH_2)$, etc., give the same metallic ion, and the rest of the molecule forms hydroxide-ion. That is to say, their hydroxides are bases and their oxides are basic. The metallic elements often enter, but only *with other elements*, into the composition of a negative ion, as is the case with manganese in $K.MnO_4$, with chromium in $K_2.Cr_2O_7$, and with silver in $K.Ag(CN)_2$.

The non-metallic or negative elements are found chiefly in negative radicals and ions. They form no nitrates, sulphates, carbonates, etc., for they could not do so without themselves alone constituting the positive ion. We have no such salts of sulphur, carbon, or phosphorus, for example. Their hydroxides, although their formulæ may be written ClO_2OH, $P(OH)_3$, $SO_2(OH)_2$, furnish no hydroxyl ions, as this would involve the same consequence. These hydroxides are divided by dissociation, in fact, so that the non-metal forms part of a compound negative radical, and the other ion is hydrogen-ion, $ClO_3.H$, $PO_3H.H_2$, $SO_4.H_2$. Their oxides are acidic. Their halogen compounds, like PBr_3 (p. 273) and S_2Cl_2 (p. 349), are completely decomposed by water. The halides of the *typical* metals are not, in general, very extensively hydrolyzed (see p. 469), and with those that are not typical, the action is readily reversible by addition of the corresponding halogen acid.

The distinction is not perfectly sharp, however, in all cases, as we have just seen with selenium and tellurium.

Classification by Atomic Weights. — Newlands (1863–4) discovered a surprising regularity that became apparent when the elements then known were placed in the order of ascending atomic weight. Omitting hydrogen (at. wt. 1) the first seven were: lithium (7), glucinum (9), boron (11), carbon (12), nitrogen (14), oxygen (16), fluorine (19). These are all of totally different classes, and include first a metal forming a strongly basic hydroxide, then a metallic element of the less active sort, then five non-metals of increasingly negative character, the last being the most active non-metal known. The next element after fluorine (19) was sodium (23), which brings us back sharply to the elements that form strongly basic hydroxides. Omitting none, the next seven elements were sodium (23), magnesium (24.3), aluminium (27), silicon (28.1), phosphorus (31), sulphur (32), chlorine (35.5). In this series there are three metals of diminishing positive character, followed by four non-metals of increasing negative activity, the last being a halogen very like fluorine. On account of the fact that each element resembles most closely the eighth element beyond or before it in the list, the relation was called the **law of octaves.** After chlorine the octaves become less easy to trace.

That this periodicity in chemical nature is more than a coincidence is shown by the fact that the **valence** and even **many physical properties,** such as the specific gravity, show a similar fluctuation in each series. In the first two series the compounds with other elements are of the types:

LiCl	GlCl$_2$	BCl$_3$	CCl$_4$;CH$_4$	NH$_3$	OH$_2$	FH
Li$_2$O	GlO	B$_2$O$_3$	CO$_2$	N$_2$O$_5$	—	—
NaCl	MgCl$_2$	AlCl$_3$	SiCl$_4$;SiH$_4$	PH$_3$	SH$_2$	ClH
Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	SO$_3$	Cl$_2$O$_7$

Thus the valence towards chlorine or hydrogen (the more familiar compound is listed in each case) ascends to four and then reverts to one in each octave. The highest valence, shown in oxygen compounds, ascends from lithium to nitrogen with values one to five, and then fails because compounds are lacking. In the second octave, however, it goes up continuously from one to seven.

Again, the specific gravities of the elements in the second series, using the data for red phosphorus and liquid chlorine, are:

• Na 0.97, Mg 1.75, Al 2.67, Si 2.49, P 2.14, S 2.06, Cl 1.33.

Mendelejeff's Periodic System.— In 1869 the Russian chemist Mendelejeff published an important contribution towards adjusting the difficulty which the elements following chlorine presented, and developed the whole conception so completely that the resulting system of classification (the **periodic system**) has been connected with his name ever since. The table on page 358 is a modification of one of Mendelejeff's, extended to include elements more recently discovered.

The chief change made by Mendelejeff from the arrangement in simple octaves is that the third series, beginning with potassium, is made to furnish material for **two** octaves, potassium to manganese and copper to bromine, and is called a **long series**. The valences fall in with this plan fairly well. Copper, while usually bivalent, forms also a series of compounds in which it is univalent. Iron, cobalt, and nickel fall between the two octaves, and cannot be accommodated in either.

Every long series contains three elements of this character, closely resembling one another. As will be seen from the table, these **transition elements**, as they are called, may be placed together in an eighth group. At the time Mendelejeff made the table, three places in the third, long series had to be left blank, as a trivalent element [Sc] was lacking in the first octave of the series, and a trivalent [Ga] and a quadrivalent one [Ge] in the second. These places have since been filled, as we shall presently see.

The fourth series, which is a long series exactly similar to the third, contained many blanks at the time of Mendelejeff, but is now nearly complete. It begins with an active alkali metal, rubidium, and ends with iodine, a halogen. The rule of valence is strictly preserved throughout the series, and in general the elements fall below those which they most closely resemble.

The fifth series is still somewhat incomplete, but the order of the atomic weights and the valence enable us satisfactorily to place most of those elements which are known. The chemical

TABLE OF THE PERIODIC SYSTEM.

The periodicity in valence throughout each series (see p. 359) is shown in the top line (E = element). The members of the same family of elements are arranged vertically. There are two families in each of the center columns, one on the left and one on the right.

	E°	E'Cl, E₂'O	E''Cl₂, E''O	E'''Cl₃, E'''O₃	E'VH₄, E'VO₂	E'''H₃, E₂VO₅	E'VH₂, E'VO₃	E'H, E₂'''O₇	E'''O₄
First (short) series	He, 4.0	Li, 6.9	Gl, 9.1	B, 10.9	C, 12.0	N, 14.0	O, 16	F, 19.0	
Second (short) series	Ne, 20.2	Na, 23.0	Mg, 24.3	Al, 27.0	Si, 28.1	P, 31.0	S, 32.1	Cl, 35.5	
Third (long) series	A, 39.9	K, 39.1	Ca, 40.1	Sc, 45.3	Ti, 48.1	V, 51.0	Cr, 52.0	Mn, 54.9	Fe, 55.8 Co, 59.0 Ni, 58.7
		Cu, 63.6	Zn, 65.4	Ga, 70.1	Ge, 72.5	As, 75.0	Se, 79.2	Br, 79.9	
Fourth (long) series	Kr, 82.9	Rb, 85.5	Sr, 87.6	Yt, 89.3	Zr, 90.6	Cb, 93.1	Mo, 96.0	...	Ru, 101.7 Rh, 102.9 Pd, 106.7
		Ag, 107.9	Cd, 112.4	In, 114.8	Sn, 118.7	Sb, 120.2	Te, 127.5	I, 126.9	
Fifth (long) series	Xe, 130.2	Cs, 132.8	Ba, 137.4	La, 139.0	Ce, 140.2	Ta, 181.5	W, 184.0	...	Os, 190.9 Ir, 193.1 Pt, 195.2
		Au, 197.2	Hg, 200.6	Tl, 204.0	Pb, 207.2	Bi, 209.0	...	...	
Sixth (incomplete) series	Nt, 222.4	...	Ra, 226.0	...	Th, 232.1	...	U, 238.2	...	

In this table atomic weights are given to the first place of decimals only.

relations to elements of the fourth series justify the position assigned to each. Cæsium, for example, is the most active of the alkali metals; barium has always been classed with strontium, and bismuth with antimony.

The sixth and last series contains only a few radioactive elements. No element with an atomic weight greater than that of uranium (238) has yet been discovered.

The most important change made in the table since the time of Mendelejeff is the addition of another group, the family of the inert gases of the atmosphere (see p. 376). These elements were unknown before 1894, but fall logically into a new group at the left hand side of the table, as here given.

General Relations in the System. — In every octave the **valence** towards oxygen ascends from one to seven, while that towards chlorine or hydrogen (see p. 356) ascends to four and then reverts to one. The long series octaves therefore exhibit the same *periodic* changes with respect to valence as do the short series octaves already discussed. Furthermore, the elements in the new group on the left hand side of the table fall directly into line with the rest by exhibiting *zero valence*. The inert gases, in other words, form no compounds with other elements. The transition elements on the right hand side of the table, similarly, justify their position by forming a few compounds in which a *valence of eight* is shown, for example "osmic acid" OsO_4. It must be admitted, however, that lower valences are more frequently displayed by these transition elements.

The **physical properties,** both of the elements themselves and of corresponding compounds, show periodic changes within the limits of each series in the same way. Thus the **melting-points** of the first eight elements in the third series are as follows:

A −188°,K 62°,Ca 810°,Sc (?),Ti 1790°,V 1720°,Cr 1520°,Mn 1280°

All of the elements in the same column do not show the same degree of resemblance, however. We find, instead, that there are *two* well-defined families in each of the columns forming the octaves. In each long series the element in the first octave falls into one of these families, the element in the second octave into

the other. In the table on p. 358 these two families are differentiated in each column by spacing one towards the left and the other towards the right of the available space. Thus in the second column of the table we have the family of the *alkali metals* (Li, Na, K, Rb, Cs) and the *copper* family (Cu, Ag, Au). The members of the first family, and their corresponding compounds, are all strikingly similar in physical and chemical properties. The members of the second family, on the other hand, have little in common with those of the first except in their valence, and even here abnormal values are shown in well-known compounds such as cupric salts, which contain the radical Cu^{II}.

The inert gases, on the left of the octaves, constitute a single family. As for the transition elements on the right, while the three members in any one series resemble one another in many respects, yet a closer relationship between elements in different series, according to the vertical arrangement shown in the table, dividing the group into three families, is also evident.

If we examine the physical properties of *successive elements,* or of corresponding compounds of successive elements, *of any one family* we find a uniform gradation observable, just as in the cases of the halogens and their hydrogen compounds studied in Chapter XIX. Thus the melting-points of the alkali metals are as follows:

<div align="center">Li 186°, Na 96°, K 62°, Rb 38°, Cs 26°.</div>

That the **chemical relations** of the elements vary just as do the physical properties of the simple substances is easily shown. Thus, each series begins with an active metallic (positive) element, and ends with an active non-metallic (negative) element, the intervening elements showing a more or less continuous variation between these limits. Again, the elements at the top are the least metallic of their respective columns. As we descend, the members of each group are more markedly metallic (in the first columns), or, what is the same thing, less markedly non-metallic (in the later columns).

The Periodic Law. — Anticipating the discovery of some more exact mode of stating the relationship in each case, and remem-

bering that similar values of each property (whether chemical or physical) recur *periodically*, usually at intervals corresponding to the length of an octave or series, the principle which is assumed to underlie the whole, the periodic law, is stated thus: **All the properties of the elements are periodic functions of their atomic weights.**

A very striking ilustration of the periodic law is presented in Fig. 88, in which atomic weights are plotted against **atomic volumes.** The atomic volume of an element is the quotient of
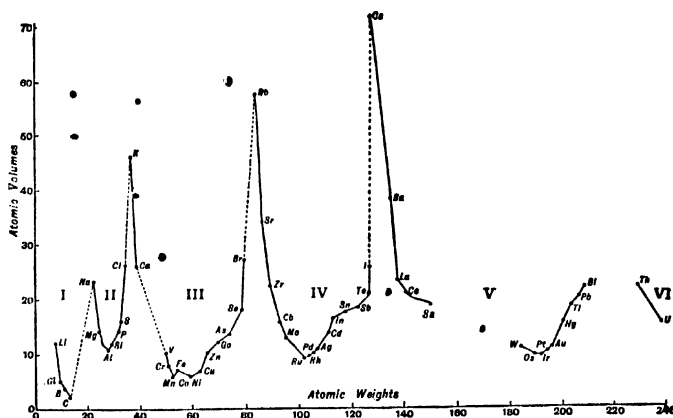
FIG. 88.

the atomic weight by the specific gravity; it is a fundamental property representing *the volumes occupied by equal numbers of atoms of different elements* (compare "atomic heat," p. 104). Strictly speaking, atomic volumes should refer throughout to elements in the solid state under the same conditions. Some of the values tabulated in the diagram are consequently not exactly comparable, since standard conditions for all the elements cannot be attained experimentally, but the periodicity of the property, first noted by Lothar Meyer, is unmistakeable. Members of the same family always occupy similar positions on the ascending or descending portions of the curve.

Applications of the Periodic System. — The system has found application chiefly in four ways:

1. In the **prediction of new elements.** Mendelejeff (1871) drew attention to the blank then existing between calcium (40) and titanium (48). He predicted that an element to fit this place would have an atomic weight 44 and would be trivalent. From the nature of the surrounding elements, he very cleverly deduced many of the physical and chemical properties of the unknown element and of its compounds. In 1879 Nilson discovered scandium (44); and its behavior corresponded closely with that predicted. Mendelejeff described accurately two other elements, likewise unknown at the time. In 1875 Lecoque de Boisbaudran found gallium, and in 1888 Winkler discovered germanium, and these blanks were filled.

2. By enabling us to decide on the **correct values for the atomic weights** of some elements, when the equivalent weights have been measured, but no volatile compound is·known (see pp. 134-135). Thus, the equivalent weight of indium was found, by experiment, to be 38.3 and, as the element was supposed to be bivalent, it received the atomic weight 76.6. It was quite out of place near arsenic (75.0), however, being decidedly a metallic element. But as a trivalent element with the atomic weight 114.8, it fell quite logically into a vacant space between cadmium and tin. Later work fully justified the change. More recently, when radium was discovered, it was found to have the equivalent weight 113 and to resemble barium. Consequently we assume that, like barium, it is bivalent, and assign it a vacant place under this element, in the last series.

3. By **suggesting problems for investigation.** The periodic system has been of constant service in the course of inorganic research, and has often furnished the original stimulus to such work as well.

For example, the first experimental determinations of the atomic weights of the *platinum metals* placed them in the order, Ir (197), Pt (198), Os (199), although the resemblance of osmium to iron and ruthenium would have led us to expect that this element should come first. For similar reasons platinum should have come last, under palladium. A reinvestigation of

the atomic weights, suggested by these considerations, was undertaken by Seubert, and the old values were found in fact to be very inaccurate. He obtained: $Os = 191$, $Ir = 193$, $Pt = 195$.

In the same way, incorrect values of many physical properties have been detected, and have been rectified by more careful work.

Originally *lead*, although it fell in the fourth column, possessed only one compound PbO_2 in which it seemed to be undoubtedly quadrivalent. Search for salts of the same form, however, speedily yielded the tetrachloride $PbCl_4$, tetracetate, and many others. The existence of osmic acid OsO_4, and a corresponding compound of ruthenium, suggests that other compounds of the elements of the eighth group, displaying the valence eight, may be capable of preparation.

4. By furnishing a comprehensive **classification of the elements,** arranging them so as to exhibit the relationships among the physical and chemical properties of the elements themselves and of their compounds. Constant use will be made of this property of the table in the succeeding chapters. Having disposed of the halogen and sulphur families, situated, respectively, in the eighth and seventh columns of the table on p. 358, we shall presently take up nitrogen and phosphorus from the right side of the sixth column. Then, from the fifth column, we shall select carbon and silicon, and from the fourth boron, leaving the other, more decidedly metallic elements for later treatment.

Defects in the Periodic System. — The periodic system is often described as if it furnished a classification of the properties of chemical substances which was complete in its scope, and ideal in its exactness. This, however, is far from being the case.

The **order of activity** of the metals (p. 240) and of the nonmetals (p. 284) summarizes many properties, and explains many features of the chemical behavior of the elements. This list is scattered through the periodic table (compare both), without any trace of regularity.

The periodic system concentrates attention too largely on *one of the valences of each element.* Thus, for manganese, it focuses attention on the septivalent form in the permanganates. But

manganous salts are more like the ferrous, the cobaltous, the chromous, and other sets of salts, none of which are in the same column of the table. Similarly, the manganic salts are like the ferric salts and the salts of aluminium. Again, copper is univalent in one series of salts, but in its better known salts it is bivalent. Silver, which belongs to the same periodic family, is always univalent, while gold, also in the same family, is univalent or trivalent, and in the latter case is almost wholly a non-metallic element. In other words, the periodic system largely ignores the variety of different classes of chemical relations which an element with several valences always shows.

The position of **hydrogen** in the system is still a matter of dispute. It is more familiar to us as a univalent positive radical, resembling the alkali metals in forming compounds with negative radicals such as chlorine, but it can also function as a univalent negative radical, resembling the halogens in forming compounds with the alkali metals, known as *hydrides*, which are salt-like in character and quite analogous to chlorides. Most chemists shelve the difficulty by giving hydrogen a position all to itself at the top of the table.

Between cerium (140) and tantalum (181.5) in the fifth series, there occur *fourteen rare elements*, called the **elements of the rare earths**, which have been omitted entirely from the Mendelejeff system. What is to be done with these elements is a point on which agreement has not yet been reached.

Finally, reference to the table will show that *in three cases* a slight displacement of the order of the elements according to atomic weights is necessary. Argon, an inert gas, is placed before potassium, an alkali metal, although its atomic weight is 0.8 higher. Cobalt is put before nickel because it resembles iron more closely. Tellurium and iodine are placed in that order to bring them into the sulphur and halogen groups, respectively. Their valence and other chemical relations both require this. These three cases constitute undoubted exceptions to the Mendelejeff system of classification. The general agreement, however, is obviously far too remarkable to be due entirely to chance.

In the final chapter it will be shown that recent work on **atomic structure** throws considerable light on the several abnor-

malities discussed above, and supplies us with a more logical
basis for the *periodicity* exhibited by the elements in respect to
valence and other properties than is furnished by the use of
Mendelejeff's system alone. Nevertheless the latter will be
found to be of valuable service to us throughout the remainder
of the book.

Exercises. — 1. Can' you explain the presence of *free* sel-
enium in the flues of pyrite burners (p. 352)?

2. How should you attempt to obtain H_2Te, and what phys-
ical and chemical properties should you expect it to possess?

3. Make a list of bivalent elements and criticize this method
of grouping as a means of chemical classification.

4. There is a blank at the end of the fifth long series, where
we should expect to find another halogen (see p. 358). If the
element that should fill this blank were to be discovered, what
would be its physical and chemical properties? What would be
the properties of its compound with hydrogen?

5. Write down the symbols of the elements in the fourth
series (that beginning with rubidium and ending with iodine)
on p. 358. Record the valence of each element toward oxygen,
using for reference the chapters in which the oxygen compounds
are described.

CHAPTER XXV

NITROGEN. THE ATMOSPHERE

IT is time now to return to the atmosphere, of which the most active component, oxygen, has already been discussed. The other chief component, nitrogen, will lead us to ammonia NH_3, and nitric acid HNO_3, both of which are of great commercial importance, and have interesting derivatives.

History of Nitrogen. — Nitrogen was recognized to be a distinct substance by Rutherford (1772), Professor of Botany in the University of Edinburgh, who named it mephitic air. Scheele showed that it was present in the atmosphere. Lavoisier recognized it to be an element, and named it *azote* (Greek, *without life*) because it did not support life. The English name records the fact that it is an important constituent of niter KNO_3.

Occurrence. — Aside from the free nitrogen, which forms nearly four-fifths of the bulk of atmospheric air, much nitrogen is found in nature in combination. Potassium nitrate KNO_3 is formed in the soil by the action of bacteria upon animal matter, and sodium nitrate $NaNO_3$ is obtained from an immense deposit in Peru and Chili. Nitrogen is an essential constituent of an important class of organic substances called the *proteins,* which are found in plants, particularly in the fruit, and in the muscles and other tissues of the animal body.

FIG. 89.

Preparation. — Nitrogen may be obtained from the air by simply removing the oxygen. This nitrogen is not absolutely pure, however, as it retains about one per cent of other gases — the "inert gases" of the atmosphere. The oxygen can be removed by allowing pieces of moist phosphorus (Fig. 89) slowly to oxidize in an en-

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closed specimen of air. The phosphoric acid H_3PO_4 and other products of the oxidation of the phosphorus dissolve in the water. For commercial purposes, nitrogen is usually prepared by passing air over heated copper (p. 38) or by fractional evaporation of liquid air (see p. 30).

Pure nitrogen can be obtained from pure compounds of nitrogen. Thus, ammonia gas may be passed over heated cupric oxide and the water vapor removed by bubbling the gas through sulphuric acid:

$$2NH_3 + 3CuO \rightarrow 3Cu + 3H_2O + N_2.$$
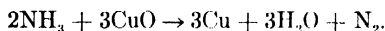
A steady stream of nitrogen is most easily made by heating sodium nitrite and ammonium chloride very gently along with a little water in a flask:

$$NaNO_2 + NH_4Cl \rightleftarrows NaCl + NH_4NO_2 \rightarrow 2H_2O + N_2 \uparrow.$$
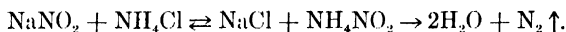
The double decomposition is reversible, and the first action might be expected to be only partially completed. But the ammonium nitrite NH_4NO_2 is unstable, and decomposes as fast as it is formed, so that the forward reaction is carried on to completion.

Physical Properties. — Nitrogen is a *colorless, tasteless,* and *odorless* gas. Its *density* is indicated in the formula N_2 (mol. wt. $2 \times 14 = 28$). It is very *little soluble* in water. When *liquefied* it is found to boil at $-194°$ and to freeze to a white solid at $-214°$.

Chemical Properties. — Nitrogen is chemically a rather indifferent gas. It unites easily with a very few elements, notably some of the *most active metals,* such as calcium and magnesium. When magnesium burns in the air, the white powder which is formed contains some of the *nitride* of magnesium Mg_3N_2, along with much of the oxide:

$$3Mg + N_2 \rightarrow Mg_3N_2.$$
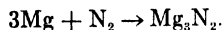
The presence of the nitride may be shown by the odor of ammonia, given off when the ash is moistened with water:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3 \uparrow .$$
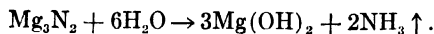
The compounds with oxygen, such as nitric oxide NO and nitric acid HNO_3, and with hydrogen such as ammonia NH_3, are of immense commercial value, but, not being very stable, they are formed only in traces by direct union of the elements. The processes for utilizing these tendencies to union, feeble as they are, for manufacturing purposes, will be described under the compounds themselves.

THE ATMOSPHERE

The components of the air may be conveniently divided into *regular* components and *accidental* components. The regular components, again, consist of three which are present in practically the same proportions in all samples, and three (namely water, carbon dioxide and dust) which vary markedly in quantity.

Components Present in Constant Proportions. — The components whose proportions are practically invariable are nitrogen, oxygen, and the group of inert gases. When the variable components are removed, the proportions of the constant ones are as follows:

	By Volume	By Weight
Nitrogen	78.06	75.5
Oxygen	21.00	23.2
Argon	0.94	1.3

The inert gases, excepting argon, are present in traces only.

The Water Vapor. — The proportion of water vapor in the air is exceedingly *variable*. When air becomes cool, the moisture *separates* in cloud and fog, which are composed of minute drops of liquid water. When much moisture is condensed, the drops are larger and fall as rain. When they fall through a cold region, they freeze to hail. When condensation takes place in air already below 0°, the fog is composed of solid and not of liquid particles. The hexagonal crystalline structures of ice which are deposited form snow.

On the other hand, when the weather becomes warm, evaporation goes on rapidly, especially in the neighborhood of seas, lakes, or moist country, and the proportion of water vapor in the air may be considerably *increased*.

Humidity. — The moisture is usually defined in terms of **relative humidity**, the standard being the quantity required to *saturate* the air at the existing temperature. A space filled with air can take up aqueous vapor only until the partial pressure of water vapor becomes equal to the vapor pressure of water (p. 75) at the same temperature. The humidity is then said to be 100 per cent. If the partial pressure actually reached is only half as great as the vapor pressure of water at the same temperature, the humidity is 50 per cent. The average humidity may be placed very roughly at about 66 per cent.

At 18°, the vapor pressure of water is 15.4 mm. (Appendix III). If the total pressure of the atmosphere were 760 mm., then the air would be saturated with moisture at 18°, and have a humidity of 100 per cent, when 15.4/760 or about 2 per cent of it by volume was water vapor. Upon cooling to 0°, at which temperature the vapor pressure of water is 4.6 mm., this air would retain only 4.6/760, or about 0.6 per cent of moisture. At 18° there would be 16.3 grams of water in a cubic meter of air and at 0° only 4.9 grams. The difference, 11.4 grams, would be precipitated as fog or rain from each cubic meter.

Test for Moisture in Air. — The presence of moisture in air may be shown by placing any deliquescent (p. 154) salt, such as calcium chloride, in an open vessel. The quantity can be measured by driving a known volume of air slowly through a weighed tube containing dry calcium chloride. It may be ascertained also by noting the temperature to which the air has to be cooled before it becomes saturated and deposits fog or dew (the *dewpoint*). For example, if air at 18° has to be cooled to 11° before it deposits dew, it contains water vapor at a partial pressure of 9.8 mm. (see Appendix III). If saturated at 18°, it would have contained water vapor under a partial pressure of 15.4 mm. Its relative humidity was therefore 9.8/15.4, or 63.6 per cent.

Moisture and Comfort. — On a moist day, we speak of the atmosphere as "heavy" or "oppressive." The barometer, however, is lower on such days, and the pressure below the average. Moist air must be lighter than dry air, because in moist air molecules of relative weight 18 (H_2O) have been substituted for an equal number of molecules of oxygen and nitrogen with the relative weights 32 and 28. The discomfort is due to a different cause. The chemical changes occurring in our bodies, and particularly the oxidation of waste and of digested food by oxygen carried by the blood, are accompanied by liberation of heat. Yet our bodies must remain at 98.4° F. (37° C.). A rise of a few tenths of a degree (F.) produces noticeable discomfort. Much of the heat is lost by radiation from the surface of the body. The extent of this loss depends upon the surface, which is invariable, and upon the surrounding temperature, which we cannot always control. Non-conducting clothes reduce the radiation, and are increased in thickness in cold weather. The real adjustment, however, is accomplished, independently of radiation, by evaporation of water at the surface of the skin. The evaporation of 1 gram of water requires about 540 calories of heat. Evaporation of a single half-ounce (14½ g.) of water will therefore lower the temperature of 76½ kilograms (168 pounds) of water (or of flesh, which is largely water) by one-tenth of a degree C. (nearly 0.2° F.).

Our comfort, then, depends upon the possibility of continual, moderate evaporation from the surface of our bodies. "Much" moisture in the air means, to us, not necessarily a great absolute amount, but a near approach to the maximum possible at the existing temperature. So the ratio of the amount present to the maximum — the humidity — is the significant fact for a practical purpose, such as feeling comfortable (or drying the wash quickly).

Ventilation. — In winter, cold air is brought into our rooms. The amount of water vapor contained in this air, even if it is saturated with moisture, is very small (see Appendix III). When this air has been heated, therefore, its *relative* humidity is too low, discomfort is felt because there is too much evaporation,

and moisture has to be added artificially. Here the moisture afforded by evaporation from our bodies has little effect on the air. In summer, however, the outside air is often already nearly saturated at the temperature of the room. At such times the speed of displacement by the ventilating appliances may not be great enough to keep the relative humidity down, and discomfort will arise from the opposite cause. To relieve it, the evaporation may be promoted by electric fans. They do not remove or add any air, but they stir it, and blow away the moist, nearly saturated, layers next to the skin.

The chief purposes of **ventilation** are, therefore, to supply fresh air, to keep it in motion, and to maintain a humidity that is neither too low nor too high.

The Carbon Dioxide. — The breathing of animals, the combustion of coal and wood, and the decay (oxidation) of vegetable and animal matter produce carbon dioxide CO_2. The same gas issues from volcanoes, and often in great quantities from the soil in regions which are no longer volcanic. The proportion in the air is therefore greatest in cities and in some volcanic regions, and least in the country and over the sea. It varies from 3.5 parts in 10,000 in the country, to 1 per cent in crowded rooms.

Its presence may be proved in any air, and very quickly in the breath itself, by bubbling the air through calcium hydroxide solution (lime-water). Calcium carbonate is precipitated (p. 424).

Carbon Dioxide and Respiration. — We draw about half a liter of air into our lungs at each breath, or half a cubic meter per hour. In the lungs some of the oxygen is removed, and some carbon dioxide is added.

	Fresh Air, Per Cent	Expired Air, Per Cent
Oxygen	21.00	15.9
Carbon dioxide	0.04	3.7

A candle flame goes out when the proportion of oxygen has fallen to 16.5 per cent. But air will sustain life until the proportion has fallen to about 10 per cent.

Nearly all experts are now convinced that the unhealthiness of over-crowded, "stuffy" rooms is not due to the increase in the proportion of carbon dioxide, which is seldom great enough to do any damage. Nor is it, due to "poisons" given off by the lungs or skin. In spite of many experiments the presence of such substances has never been proved—they are imaginary. The harm is caused by the *stillness* of the air, which, as we have seen (p. 371), prevents the removal of the water vapor near the skin, and therefore hinders evaporation.

Dust in the Air. — A beam of sunlight crossing a dark room can be seen by the light reflected from the particles of dust which all air contains. These are chiefly solid bodies, and are composed of salts, limestone, clay, and other rock materials, of soot and other particles of unburnt fuel, of bits of hay or straw, and of fragments of insects and other débris of plants and animals. They also include living particles, such as bacteria, and spores of plants such as moulds. The latter, when they settle upon food, germinate and give rise to putrefaction. Some of the bacteria also produce disease, when they enter the body at a place where the skin has been damaged by a cut or burn.

It is instructive to note that natural soil contains about 100,000 micro-organisms, and good, unfiltered river water from 6000 to 20,000, in each cubic centimeter. Ordinary, pure air contains only 4 to 5 micro-organisms per liter. Most of these bacteria come from the drying of soil and the dispersion of the resulting dust.

If dust were not present, we should soon notice its absence. There would be no clouds or rain. It appears that moisture will not condense to fog or rain in air which has been filtered, by being drawn through a wide tube containing a long (20 inches or more) plug of cotton, and has so been freed from dust. The particles act as nuclei, round which the liquid grows at the expense of the vapor. In the absence of dust, the condensation would occur directly upon the surfaces of plants, houses, and animals. Thus, in a dustless atmosphere, an open shed or shelter, or an umbrella, would afford no protection whatever against a wetting.

The formation of fog from ordinary air, and its non-forma-
tion in filtered air are easily shown in a darkened room (Fig. 90).
The flask contains water to
saturate the air. When the
tube leading to the water
pump is opened for an in-
stant, the saturated air in
the flask expands and is
cooled (see p. 374). In such
circumstances, ordinary air
gives a fog, brilliantly illu-
minated by the beam of
light, while filtered air
(dustless) gives none.

TO PUMP
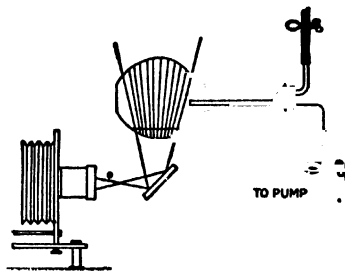
FIG. 90.

Air a Mixture. — The air does not contain in combined con-
dition the various substances we have named. Each of the
substances in air shows precisely the same properties which it
exhibits when free, separate, and pure. This behavior is charac-
teristic of a *mixture*.

Thus, the observed *density* of the air is precisely that which
we find by calculation from the known proportions and several
densities of the components. The *solubility* of each gas is ob-
served to be the same as if it were alone present.

Again, when *liquefied air* is allowed to *evaporate* in a suitable
apparatus, the nitrogen, being more volatile, can be separated
almost *completely* from the oxygen. When the oxygen is, in
turn, allowed to evaporate, the carbon dioxide and water remain
as solids, frozen by the low temperature.

Finally, the *exact proportions cannot be represented by a
chemical formula*. This shows that the law that, in chemical
compounds, the proportions can be represented by multiples of
the atomic weights by whole numbers (p. 99), does not apply to
air, and air is consequently not a chemical compound.

In spite of the fact that air is a mixture, the composition of
the air is remarkably uniform and constant. The uniformity is
due to constant mixing by the winds. The steadiness of the
composition from year to year is due to the fact that, although

decay and combustion continually remove oxygen and add carbon dioxide, vegetation as continually consumes the latter and restores the former (p. 512). The mass of carbon dioxide in the whole atmosphere of the planet, about 2450 thousand million tons, is so great that the amounts added and removed by the agencies just mentioned are small by comparison.

Liquefaction of Air. — The principle now used in liquefying gases depends on the fact that, although a perfect gas, when expanding into a vacuum, should suffer no fall in temperature, since it does no work, ordinary gases do become cooled very slightly. The work which they do in expanding in such circumstances is done in overcoming the slight cohesion between their molecules (p. 54), so that a forcing apart of molecules to greater distances from one another, which consumes heat, has to take place. Since this cohesion becomes more conspicuous the lower the temperature, the cooling effect of expansion becomes greater and greater as the temperature falls.

Liquid air is now extensively prepared as a source of pure oxygen or nitrogen for use in chemical industry. The air is first freed from carbon dioxide by means of lime. It is then compressed to 200 atmospheres, the heat of compression being counterbalanced by passing through pipes cooled with running water. This compression condenses most of the water vapor present in the air, the last traces of water and of carbon dioxide being removed by solid sodium hydroxide. The air then passes into the liquefier.

In Hampson's apparatus (Fig. 91) this consists essentially of two concentric copper pipes, about 130 meters in length, coiled closely in a cylindrical form, with non-conducting covering to prevent access of heat. The compressed air is forced in through the inner pipe
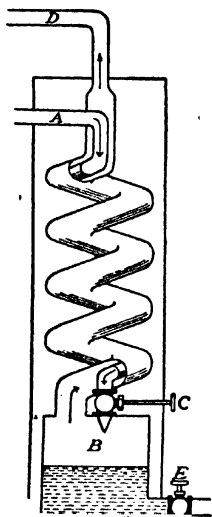
Fig. 91.

A. When it reaches the extremity of this pipe, it suddenly escapes into a closed vessel *B* through a minute opening controlled by the valve *C*. This expands it to 1 atm. pressure and lowers its temperature. The air can now escape only by traveling back through the outer pipe *D* to the final exit near the top. In doing so, it cools the highly compressed air in the inner pipe. This cooler air, on reaching the closed vessel, expands and becomes colder than ever, and in passing backwards lowers the temperature of the air in the inner pipe still further. Finally, the air in this pipe liquefies, and drops of liquid air are expelled into the closed vessel. The liquid air is allowed to run out through a valve *E*, from time to time, as it accumulates.
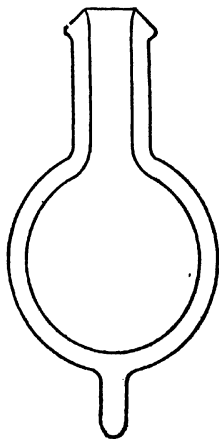
Liquid air can be kept in Dewar flasks (Fig. 92). The space between the inner and outer flasks is evacuated, so that there is no gas to carry heat from the atmosphere in to the liquid air. The inner surface of the outer flask is often silvered, so that radiant heat, from surrounding bodies, may be reflected and not absorbed. Similar containers are in common use for keeping liquids hot or cold for a long time (Thermos flasks).

Fig. 92.

Liquid Air. — Liquid air varies in composition, as the nitrogen (b.-p. $-194°$) is less condensible than the oxygen (b.-p. $-182.5°$). When liquid air evaporates, therefore, the first portions of gas that come off consist almost entirely of *nitrogen.* Nitrogen obtained in this way is used in the manufacture of ammonia by the Haber process (p. 380), and in the formation of calcium cyanamide (p. 505). By allowing evaporation to continue a liquid containing 75 to 95 per cent of oxygen is obtained (compare p. 30). It contains about 3 per cent of argon, and is a convenient source of this element. Cartridges made of granu-

lar charcoal and cotton waste, when saturated with oxygen-rich liquid air, are used as an *explosive* in mining.

THE INERT GASES

Argon A. — Cavendish (1785) sought for other gases in air by adding more oxygen, passing an electric discharge to cause this gas to combine with the nitrogen, and absorbing the product (NO_2) in potassium hydroxide solution. He found that only about 0.8 per cent of inactive gas remained. Since the quantity, was so small, and the spectroscope, by which the gas even in small amounts would have been recognized to be new, was not invented until much later, he did not pursue the subject.

A century later, Lord Rayleigh observed that, while speci- mens of oxygen and other gases made purposely from various sources always had the same density, nitrogen was an exception. One liter of nitrogen made from air, and supposed to be pure, weighed 1.2572 g. When the gas was manufactured by decom- position of five different compounds, such as urea and certain oxides of nitrogen, the mean weight of a liter of this nitrogen was only 1.2505 g. The difference, amounting to nearly 7 mg., was very much greater than the experimental error. The sus- picion naturally arose that some heavier gas was present in natural nitrogen. In 1894 Ramsay, in consultation with Ray- leigh, succeeded in separating this gas by passing the "nitrogen" repeatedly over heated magnesium, and so removing the real nitrogen as solid magnesium nitride Mg_3N_2. The remaining gas, about 1 per cent of the whole, was named **argon** (Greek, *lazy* or *inactive*), because it would combine with no other element.

Argon has a *molecular weight* of 39.9 (nitrogen only 28), and when liquefied *boils* at $-186°$ and *freezes* at $-189.5°$. It is used in filling electric light bulbs.

Helium He. — In 1868 Lockyer first detected an orange line in the spectrum of the sun's prominences which was not given by any terrestrial substance then known. The line was so con- spicuous that it was attributed to the presence of a new chemical element, which was named **helium** (Greek, *the sun*). Ramsay, in
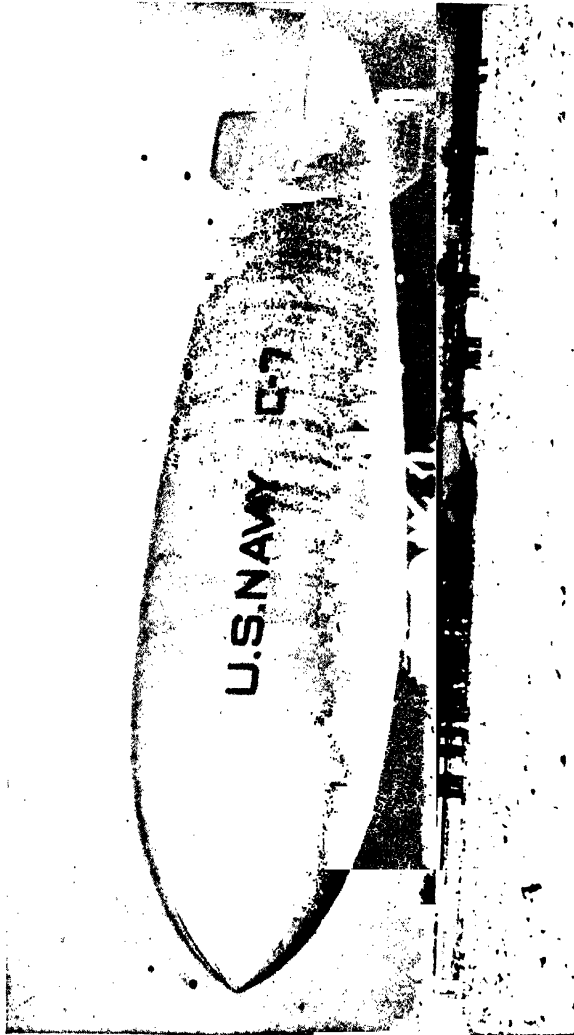
THE FIRST HELIUM-FILLED DIRIGIBLE AFTER ITS LANDING AT WASHINGTON

searching for sources of argon, examined a gas which Hillebrand had obtained from uraninite, an ore of uranium. He was surprised to find (1895) that it contained a large proportion of a very light gas, the spectrum of which was identical with that of solar helium. The same gas is found in very minute amounts in the atmosphere. The *molecular weight* of helium is 4.00, so that it is only twice as dense as hydrogen. It was the last gas to be liquefied (by Onnes), and the liquid *boils* at $-268.7°$ ($4.3°$ Abs.). Like argon, it does not enter into chemical combination. This very unsociability of helium, however, renders it the ideal gas for balloons and avoids all the risk of fire or explosion attendant upon the use of hydrogen. Helium exists in small quantity in many natural gases (see p. 434), and is obtained pure by liquefying out the other components.

Other Inert Gases. — When liquefied argon was allowed to evaporate, the first vapor coming off was found to contain another gas, **neon** (Greek, *new*; mol. wt. 20.2), along with helium. Careful distillation of the remaining liquid gave two other gases, **krypton** (Greek, *hidden*; mol. wt. 82.92) and **xenon** (Greek, *stranger*; mol. wt. 130.2). The total amount of these four gases, however, was only 1 part in 80, the remaining 79 parts being pure argon.

Chemical Relations of the Inert Gases. — None of these gases forms any compounds. They do not combine with themselves even, as do the more common gases such as H_2, O_2, Cl_2. The molecule in each case is *monatomic*, for example He, A. The valence throughout the group is therefore zero.

Niton (radium emanation; see p. 723), with a molecular weight of 222.4, also belongs to the family of inert gases.

Exercises. — 1. Does the removal of oxygen from air by means of phosphorus (p. 366) prove that air is a mixture?

2. What are the radicals of sodium nitrite, and what are their valences? Justify the nomenclature.

3. At 77° F. the air of a room contains water vapor at a partial pressure of 20 mm. What is the percentage of humidity?

4. What weight of water is contained in a cubic meter (1000 liters) of air saturated at 10° C.?

5. Air at 18° has to be cooled to 14° before it deposits dew or fog. What is the percentage humidity?

6. Why is the air nearest the ground heated (by the sun) to a higher temperature than the upper air?

7. Formulate a method for the complete *quantitative* analysis of air.

8. What is the valence of nitrogen in ammonia NH_3 and in nitric acid HNO_3?

9. A sample of moist air, confined over water at 15° and 760 mm., occupies 15 c.c. It is mixed with 20 c.c. of hydrogen, and the mixture is exploded, and suffers a contraction of 9.5 c.c. What would be the volume of the oxygen it contained if measured dry at 0° and 760 mm.?

AMMONIA

T interest in ammonia centers largely in the use of lique-
fied ammonia for refrigeration, in the employment of the gas in
making carbonate of soda (see p. 491), and in the value of its
compounds as fertilizers and explosives.

Manufacture. — Ammonia is formed when nitrogenous or-
ganic matter is heated, in absence of air. It was formerly made
by distilling scraps of hoofs, horns, and hides. The solution of
the gas thus obtained was called "spirit of hartshorn." The
pungent odor of smoldering feathers, leather, or fur is, therefore,
partly due to its presence in the escaping vapors. From the
proteins of the original plants, **coal derives** a considerable propor-
tion of nitrogenous matter. Hence, when coal is distilled for the
making of coal gas, or, on a far larger scale, for the making of
coke, much ammonia can be separated, by washing with water,
from the mixture of gases produced. The aqueous solution is
separated from the tar, neutralized with sulphuric acid, and
evaporated to give the salt, ammonium sulphate $(NH_4)_2SO_4$.

$$NH_3 + H_2O \rightarrow NH_4OH \text{ (ammonium hydroxide).}$$
$$2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O.$$
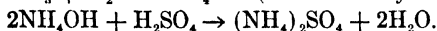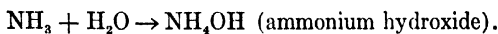
The distillation of coal is the chief source of commercial am-
monia. In the United States, prior to the war, nearly all the
coke was made in "beehive" ovens, in which the vapors issuing
from the coal are burned, uselessly, on the spot. Since the war,
about 75 per cent of coke is made in "by-product" coke ovens,
in which the ammonia and innumerable other by-products are
collected and utilized (see p. 538). In Scotland, oil-bearing
shale is distilled for the purpose of extracting the petroleum, and

much ammonia, liberated at the same time, is collected. Formerly it was allowed to escape, but, in the absence of a protective tariff, the competition of petroleum from American and Russian wells compelled economy. Now, the profit on the sale of the ammonium sulphate pays the whole cost of mining and distilling the shale.

Synthetic Ammonia. — The latest method of manufacturing ammonia is by the direct union of hydrogen and nitrogen. Exactly the same difficulties are encountered in the commercial operation of this reaction (**Haber's process**) as in the manufacture of sulphur trioxide by the contact process (p. 336), but in a greatly accentuated form. The union of the gases, which is exothermic, is exceedingly slow in the absence of a suitable catalyst:

$$N_2 + 3H_2 \rightarrow 2NH_3 + 24{,}000 \text{ calories.}$$
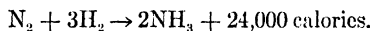
In the presence of a *contact agent* — such as a specially prepared mixture of iron and molybdenum — combination is greatly hastened. Traces of other gases, however, such as carbon monoxide or hydrogen sulphide, must be very carefully eliminated from the reacting mixture, since they act as *poisons* on the catalyst, that is, they destroy or impair its activity.

The reaction is reversible, and much more incomplete than is the union of sulphur dioxide and oxygen under similar conditions. Since the forward action evolves heat, the reverse action is favored by raising the temperature (Van't Hoff's law, p. 216), hence the yield of ammonia in the equilibrium mixture becomes less and less the higher the temperature employed. Thus, under one atmosphere pressure, the proportions of the gases that combine in a mixture of one volume nitrogen and three volumes hydrogen are as follows: at 200°, 15.3 per cent; at 300°, 2.2 per cent; at 500°, 0.13 per cent; at 1000°, 0.004 per cent.

The preponderance of this reverse reaction, or in other word the tendency of ammonia to decompose into its constituer elements as the temperature is raised, makes it impossible t obtain high yields of ammonia by the Haber process at hig

temperatures, while at lower temperatures the combination is too tardy, even in the presence of a catalyst. Fortunately we are able to make use of another of our general laws, the principle of Le Chatelier (p. 218), to improve matters. It will be noted from the equation given above that the union of hydrogen and nitrogen to form ammonia is accompanied with diminution of volume, 1 volume of nitrogen + 3 volumes of hydrogen = 2 volumes of ammonia. Consequently *the forward action will be favored by increase of pressure*. In fact, under 200 atmospheres pressure the yield of ammonia in the equilibrium mixture is as follows: at 200°, 86 per cent; at 500°, 17.6 per cent; at 600°, 8.2 per cent; at 1000°, 0.9 per cent.

There still remains the question of speed of combination. This decreases very rapidly as the temperature is lowered (compare p. 215), and no catalyst has yet been prepared which is sufficiently active to make the combination of nitrogen and hydrogen speedy enough to permit the process to be operated on an industrial scale much below 600°. A yield of about 8 per cent ammonia, therefore, is the best that can be obtained.

Details of the Haber Process. — The hydrogen may be obtained either as a by-product in an electrolytic process (p. 170), or by the action of steam on iron (p. 60), or by careful purification of water-gas (see p. 427). The preparation of pure hydrogen, it may be noted, is the most costly feature of the whole process. The nitrogen is obtained from liquid air. After removal of all impurities injurious to the catalyst, the mixed gases are passed under high pressure into the vessel containing the catalyst. This consists of a steel "bomb" specially adapted to withstand the enormous pressure. Very serious disasters have taken place owing to the explosion of such bombs. After passing over the catalyst, the reaction mixture is cooled and its ammonia content (6 to 8 per cent) removed either by refrigeration or by absorption in water. The residual nitrogen and hydrogen are returned to the plant for further treatment.

The ammonia obtained is used, in times of peace, mainly in the manufacture of *fertilizers*, such as ammonium sulphate. In

war times, however, it is required more urgently for the production of *explosives*. Nitric acid HNO_3, which is necessary in the preparation of most explosives, is obtained from ammonia by oxidation (see p. 395). By the neutralization of nitric acid with ammonia, ammonium nitrate NH_4NO_3 is formed. A mixture of this substance with trinitrotoluene (p. 598) was used extensively as a high explosive during the Great War, under the name of **amatol**.

Synthetic ammonia may also be prepared by the calcium cyanamide process (see p. 505). But for these two processes, Germany would never have been able to continue fighting in the Great War beyond the first year. With all foreign supplies of nitrates (Chili saltpeter) cut off, the only other available source of ammonia was the by-product coke industry, and this was already being utilized almost to its maximum. In the allied countries, unfortunately, the Haber process during the war was not developed beyond the experimental stage.

The productive capacity of Haber process plants in 1920 was no less than one and a half million tons (calculated as ammonium sulphate).

Preparation in the Laboratory.— In the laboratory, ammonia is most readily made by heating a mixture of a salt of ammonium, such as the chloride (NH_4Cl) or sulphate, and slaked lime $Ca(OH)_2$.

FIG. 93.

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_4OH \rightarrow 2NH_3 + 2H_2O.$$
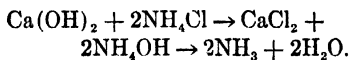
The ammonium hydroxide, formed by the double decomposition, immediately decomposes. To free the gas from water vapor, it is passed through a tower filled with quicklime CaO (Fig. 93).

Sometimes, a stream of the gas is generated by warming commercial ammonium hydroxide solution (*aqua ammonia*), an
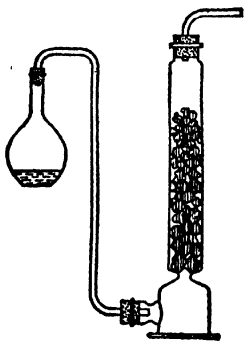
drying the gas as above. Liquefied ammonia is obtainable in small iron cylinders, and is a convenient source when much of the gas is required.

The liberation by hydrolysis of nitrides, already noted (p. 367), is interesting:

$$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3.$$
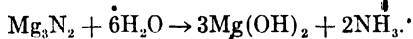
Physical Properties. — Ammonia is a *colorless* gas. It has a soapy *taste*, and a very pungent *odor*. Its *density*, recorded in the formula NH_3, indicates that it is only about half as heavy as air. It is easily *liquefied*, boiling at $-38.5°$, and exerting a pressure of 6 atmospheres at $10°$. The gas is exceedingly *soluble* in water (1 vol. water dissolves 1300 vol. of NH_3 at $0°$). A 35 per cent solution is sold as "concentrated ammonia."

The extreme solubility in water may be shown by the "fountain" experiment (Fig. 94). The flask is filled with ammonia by downward displacement of air. The long tube is closed by a short rubber tube and a clip at the bottom (not shown). The "dropper" contains water, and is closed at the tip with soft wax. A few drops of water, squirted into the flask by pinching the "dropper," dissolve at once so much of the gas that the water rushes in, like a fountain, through the longer tube, when the clip is opened. Under the best conditions the flask will be almost completely filled.

Fig. 94.

Liquefied ammonia is **used in refrigeration.** In evaporating at $-33°$ it absorbs 330 cal. per gram. Water alone, among common liquids, has a greater heat of vaporization. The large amount of heat is, in both cases, required because of the relatively large volume of the vapor (due to low molecular weight)
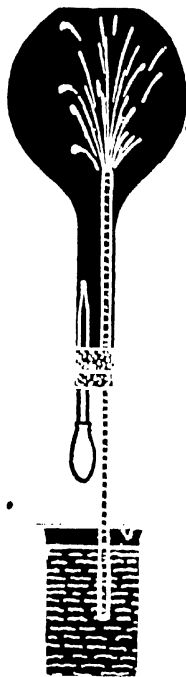
and to the fact that both liquids are associated (p. 145) and the decomposition of the complex molecules absorbs heat. To freeze 1 gram of water at 0°, 79 cal. have to be removed. Thus 1 g. of liquid ammonia will convert 4 g. of water into ice. Fig. 95 shows one arrangement diagrammatically. The ammonia gas, obtained from a cylinder of liquid ammonia, is driven by the pump F along the tube E and is liquefied in the tube coiled in the tank AB. Cold water circulating through AB removes the heat produced by the compression and liquefaction of the gas. The liquid ammonia is allowed to drip through the stopcock G into the lower coil, and there it evaporates. In doing so, it takes heat from a 30 per cent solution of calcium chloride in water. This cooled brine leaves the tank at D, circulates through another tank, in which water-filled ice molds are suspended, and returns to C. When used for cooling storage-rooms for meat, the brine circulates through pipes in the same way. The machine is constructed of iron, because copper and brass are corroded by ammonia.
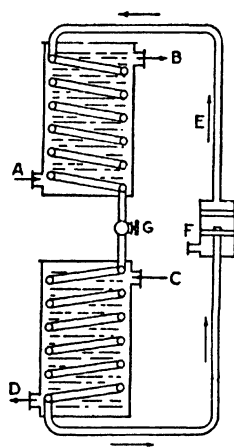
Fig. 95.

Chemical Properties. — Ammonia, as we have seen, is not very **stable**, and decomposes rapidly and almost completely at 700°. A discharge of sparks from an induction coil (temperature about 2000°) has the same effect, so that a sample of the gas, confined over mercury in a closed tube (Fig. 96), may be shown to double in volume by continued sparking. Every two molecules give four:

$$2NH_3 \rightleftarrows 3H_2 + N_2.$$
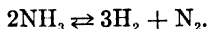
Ammonia **reduces** many oxides, when the latter are heated and the gas is lead over them:

$$\cdot \; 3CuO + 2NH_3 \rightarrow 3Cu + 3H_2O + N_2.$$
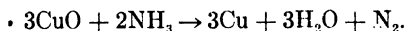
Ammonia burns in pure oxygen (not in air) to give steam and nitrogen.

Chlorine and bromine (vapor) combine with the hydrogen and liberate nitrogen:

$$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl. \cdot$$
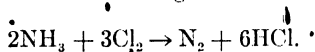
When **metals** capable of uniting with nitrogen (p. 367) are heated in a stream of ammonia gas, hydrogen is displaced. Magnesium gives magnesium nitride:

$$\cdot \quad 2NH_3 + 3Mg \rightarrow Mg_3N_2 + 3H_2.$$
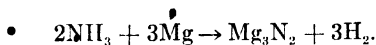
Sodium and potassium, however, give amides (compounds containing the group NH_2), such as sodamide $NaNH_2$:

$$2NH_3 + 2Na \rightarrow 2NaNH_2 + H_2.$$
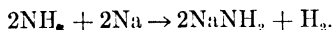
The most striking property of ammonia is that it **combines with acids,** giving ammonium salts. It **combines also with water** at low temperatures to give ammonium hydroxide NH_4OH and ammonium oxide $(NH_4)_2O$, white solids melting around $-80°$. These compounds are unstable at ordinary temperatures, so that a solution of the gas, in a great excess of water, is the only form of ammonium hydroxide convenient for use:

FIG. 96.

$$NH_3 + H_2O \rightleftarrows NH_4OH.$$
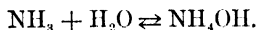
Ammonium Hydroxide. — This substance, as indicated by the way in which we have written its formula, is a **base.** The ions are $(OH)^-$, given by all bases, and $(NH_4)^+$, ammonium-ion, which is found also in the salts mentioned above. The latter is a compound positive radical, playing the part of a univalent metallic element, such as Na or K.

As a base, ammonium hydroxide, although rather weak (little ionized), turns red litmus blue, possesses the characteristic soapy
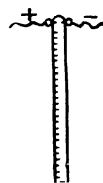
tasb and feeling, and enters into double decomposition with acids, neutralizing them:

$$NH_4OH + HCl \rightarrow H_2O + NH_4Cl.$$
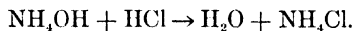
The salts, obtained by evaporation, are, of course, identical with those formed by union of ammonia with the same acids.

Ammonium hydroxide used to be known as "volatile alkali," in reference to the fact that it decomposes into its constituents $(NH_3 + H_2O)$, both of which are volatile, while the other alkalies (NaOH, etc.) are not volatile ("fixed"). This property was utilized in the laboratory method of making ammonia (p. 382). Ammonium hydroxide solution is sold under the name of **household ammonia**, and is used, in washing and cleaning, to soften the water.

The Salts of Ammonium. — The salts are all highly ionized in aqueous solution, giving NH_4^+ as the positive ion:

$$(NH_4)_2SO_4 \rightleftarrows 2NH_4^+ + SO_4^=.$$
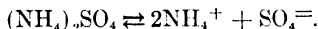
When *heated,* dry, in a tube, they are decomposed. Most of them give ammonia and the acid. When the latter is volatile, the whole material of the salt is thus converted into gas. The acid and the ammonia reunite to form the solid salt when the vapor reaches a cool part of the tube (sublimation, p. 276):

$$NH_4Cl \text{ (solid) } \rightleftarrows NH_4Cl \text{ (gas) } \rightleftarrows HCl + NH_3.$$

The **test** for ammonium salts is to warm them dry or in solution, with a base, when the *odor of ammonia* becomes noticeable.

$$\left.\begin{array}{l}(NH_4)_2SO_4 \leftrightarrows SO_4^= + 2NH_4^+ \\ 2KOH \leftrightarrows 2K^+ + 2OH^-\end{array}\right\} \leftrightarrows 2NH_4OH \rightleftarrows 2H_2O + 2NH_3 \uparrow.$$
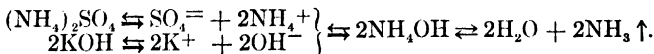
When the solution is used, it is the tendency of the NH_4^+ and OH^- to unite to form the slightly ionized, molecular hydroxide that sets the other equilibria in motion.

In ammonium salts, the nitrogen is quinquivalent.

Other Compounds of Nitrogen and Hydrogen. — **Hydrazine** N_2H_4 bears the same relation to ammonia as hydrogen peroxide

H_2O_2 does to water. Its aqueous solution is alkaline, and salts are formed by neutralization. **Hydrazoic acid** HN_3 is a violently explosive liquid, with acid properties.

Halogen Compounds of Nitrogen. — When ammonium chloride solution is treated with excess of chlorine, drops of an oily liquid, **nitrogen trichloride,** are formed: $3Cl_2 + NH_4Cl \rightarrow NCl_3 + 4HCl$. It is extremely explosive, resolving itself into its constituents with liberation of much heat.

When a solution of iodine in potassium iodide solution (p. 276) is added to aqueous ammonia, a brown precipitate is formed. This at ordinary temperatures has the composition NH_3,NI_3, and is commonly named **nitrogen iodide.** It may be handled while wet. When dry, if touched with a feather, it decomposes into its constituents with violent explosion.

Exercises. — 1. Why can we not dry ammonia gas with concentrated sulphuric acid or with phosphorus pentoxide?

2. How many grams of water at $0°$ could be frozen (p. 73) by the removal of the heat required to evaporate 50 g. of liquid ammonia?

3. How many grams of ammonia are contained in 1 l. of "concentrated ammonia" (p. 143)?

4. What are the ions of hydrazine hydrate? Formulate (p. 258) the neutralization of this base with sulphuric acid.

5. How could you separate a mixture of oxygen and ammonia?

6. Classify (p. 168), (a) the interaction of a nitride with water (p. 383) and (b) of chlorine and ammonium chloride (p. 387), (c) the results of heating ammonium nitrite (p. 367) and (d) ammonium chloride (p. 386).

7. Why does not ammonia burn in air (p. 385)?

8. What substances are present in ammonium hydroxide solution? When the liquid is heated, what happens to each? Formulate the system.

CHAPTER XXVII

OXIDES AND OXYGEN ACIDS OF NITROGEN

THE names and formulæ of the oxides and oxygen acids of nitrogen are as follows:

Nitrous oxide N_2O ←→   Hyponitrous acid $H_2N_2O_2$
Nitric oxide NO
Nitrous anhydride N_2O_3 ←→   Nitrous acid HNO_2
Nitrogen tetroxide $N_2O_4 \rightleftarrows 2NO_2$
Nitric anhydride N_2O_5 ←→   Nitric acid HNO_3.

All the oxides are endothermal compounds (p. 202), yet, with the exception of the third and the last, they are all relatively stable. The acids, when deprived of the elements of water, yield the oxides opposite which they stand (p. 311). Conversely, excepting in the case of nitrous oxide, the anhydrides with water give the acids. All of these substances are made directly or indirectly from nitric acid — nitric anhydride by removal of water, the others by reduction. We turn, therefore, first, to nitric acid and its properties.

NITRIC ACID HNO_3

Nitric acid HNO_3 is used in large quantities for making explosives like guncotton, picric acid and TNT, and plastics like celluloid, as well as innumerable drugs and dyes. Nitrates are largely used as fertilizers (p. 526).

Manufacture. — Nitric acid is obtained in two ways, namely, by the action of sulphuric acid upon natural sodium nitrate and by oxidation of the nitrogen of the atmosphere. The processes which utilize the latter method will be referred to in a later section.

Sodium nitrate, Chile saltpeter, is found in an immense de-

posit (2 by 220 miles) on the boundary of Chile and Peru. This salt is mixed with concentrated sulphuric acid in iron retorts and gently heated to drive off the nitric acid. The sodium-hydrogen sulphate remains in the retort:

$$NaNO_3 + H_2SO_4 \rightleftarrows NaHSO_4 + HNO_3 \uparrow.$$
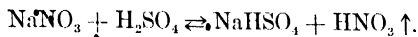
The vapor is condensed in glass tubes (cooled with water) and the acid collected in vessels of earthenware. Sulphuric acid (b.-p. 330°) is used because it is much less volatile than nitric acid, and so only the latter is vaporized. The acid boils at 86° (760 mm.), but, to prevent loss by decomposition, a lower
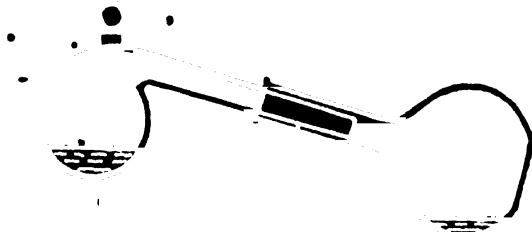
Fig. 97.

boiling-point is secured by reducing the pressure in the whole apparatus.

In the laboratory the same action is employed, without, however, the reduction in the pressure (Fig. 97).

Physical Properties. — Pure hydrogen nitrate (100% HNO_3) is a colorless, mobile liquid (sp. gr. 1.52) boiling at 86°, and freezing to a solid (m.-p. − 47°). It fumes strongly when its vapor issues into moist air (compare p. 161). An aqueous solution containing 68 per cent of the substance boils at 120.5°, while the pure acid, pure water, and all other mixtures, boil at lower temperatures. This 68 per cent nitric acid of constant boiling-point (p. 166) forms the "concentrated nitric acid" of commerce (sp. gr. 1.41).

Chemical Properties. — 1. Like chloric acid (p. 309), and other oxygen acids of the halogens, nitric acid is most stable when

mixed with water. The pure acid **decomposes** while being distilled:

$$4HNO_3 \rightarrow 4NO_2 + 2H_2O + O_2,$$
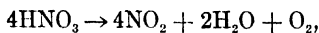
yet not with explosive violence like chloric acid. The distillate is colored brown by dissolved nitrogen tetroxide NO_2 ("fuming" nitric acid). Repeated distillation finally leaves 68 per cent of the acid, mixed with 32 per cent of water formed by the above decomposition. The acid of constant boiling-point is, therefore, reached, as usual, from more concentrated as well as from less concentrated specimens.

2. Nitric acid, when dissolved in water, is highly ionized, and is therefore active as an **acid**. By interaction with hydroxides and oxides it forms nitrates.

3. When pure nitric acid (b.-p. 86°) is poured upon' phosphoric anhydride, the latter combines with the elements of water, and distillation gives **nitric anhydride**: $2HNO_3 + P_2O_5 \rightarrow N_2O_5 \uparrow + 2HPO_3$. The anhydride is a white solid melting at 30° and boiling at 45°. It unites vigorously with water to form nitric acid. It decomposes spontaneously into nitrogen tetroxide and oxygen: $2N_2O_5 \rightarrow 4NO_2 + O_2$.

4. Like the unstable oxygen acids of the halogens, nitric acid is an **oxidizing agent** even when diluted with water. The multiplicity of the products into which it may be decomposed by reduction, however, renders separate treatment of this property necessary (see p. 396).

5. Nitric acid interacts energetically with many compounds of carbon to give **nitro-derivatives**. Many of these are of great importance as explosives. Their preparation and properties will be discussed in a later chapter (pp. 596-598).

6. Nitric acid produces substances of bright-yellow color, known as **xanthoproteic acids**, when it comes in contact with proteins, *e.g.*, in the skin, or in wool. Hence nitric acid stains woolen clothing yellow. This reaction is used as a test for proteins.

Nitrates. — The nitrates are all more or less easily soluble in water. When heated they decompose in one or other of three

ways (see pp. 392, 398, 400). The individual nitrates, such as sodium nitrate and potassium nitrate, are described elsewhere.

NITRIC OXIDE AND NITROGEN TETROXIDE

Preparation of Nitric Oxide NO. — Pure nitric oxide is obtained by adding nitric acid to a boiling solution of ferrous sulphate in dilute sulphuric acid:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \rightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$
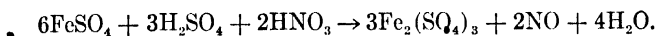
This action is used as a means of determining the quantity of nitric acid in a solution, or of nitrates in a mixture, by measurement of the volume of nitric oxide evolved.

Nitric oxide may also be obtained when sufficiently dilute nitric acid (sp. gr. 1.2) acts upon copper (see p. 397). This interaction furnishes the most convenient method of generating the gas in the laboratory (see also p. 393).

Properties of Nitric Oxide. — Nitric oxide is a colorless gas. In solid form it melts at $-167°$, and the liquid boils at $-153.6°$. Its solubility in water is slight. The density of the gas shows the formula to be NO; and there is *no* tendency to form a polymer, such as N_2O_2, even at low temperatures.

This gas is the most stable of the oxides of nitrogen. Vigorously burning phosphorus continues to burn in the gas, nitrogen being set free. Burning sulphur and an ignited taper, however, are extinguished.

Nitric oxide has two characteristic chemical properties. It unites directly with oxygen in the cold to form the reddish-brown nitrogen tetroxide:

$$2NO + O_2 \rightleftarrows 2NO_2.$$
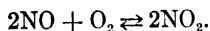
The same result follows when it is led into warm concentrated nitric acid: $NO + 2HNO_3 \rightleftarrows 3NO_2 + H_2O.$

It also forms unstable compounds with a number of salts, the compound in the case of ferrous sulphate, $FeNO.SO_4$, being capable of existence in cold aqueous solution and possessing a brown color. Since ferrous sulphate will first reduce nitric acid

to nitric oxide (p. 391), and the excess of the salt will then give a brown color with the product, a delicate **test for nitric acid** (**or** nitrates) is founded upon these actions.

Preparation of Nitrogen Tetroxide NO_2. — This substance is liberated by heating nitrates, other than those of potassium, sodium, or ammonium, such as lead and copper nitrates:

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

The oxide of the metal remains, unless this oxide is itself decomposed by heating (p. 65). When the mixed gases are led through a **U**-tube immersed in ice, the tetroxide condenses as a yellow liquid (b.-p. 22°, m.-p. – 10.5°), and the oxygen passes on.

The compound may also be made by direct union of nitric oxide and oxygen, or by oxidation of nitric oxide by concentrated nitric acid (p. 391). It is likewise almost the sole product of the interaction of *concentrated* nitric acid with tin or copper (see p. 397).

Properties of Nitrogen Tetroxide. — The most striking peculiarity of this gas is that, when hot, it is deep brown in color, and when cold, pale yellow. The density of the brown gas, at 156°, corresponds to the formula NO_2, that of the yellow gas at 22° to N_2O_4. At intermediate temperatures equilibrium mixtures of the two molecular species exist. When the temperature is carried above 156°, by passing the brown gas through a hot tube, the brown color begins to disappear, and nitric oxide and oxygen are formed. This decomposition is complete, however, only above 600°. On cooling, the same steps through brown gas to pale-yellow gas are retraced:

$$2NO + O_2 \rightleftarrows 2NO_2 \rightleftarrows N_2O_4$$
Colorless   Brown   Pale Yellow
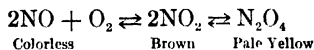
Since nitrogen tetroxide yields free oxygen more readily than does nitric oxide, phosphorus burns readily in it; a taper, however, is extinguished. On account of its oxidizing power, it is sometimes used in bleaching flour.

The most interesting property of nitrogen tetroxide is its

action upon water, whereby nitric acid is formed, and nitric oxide escapes:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO.$$
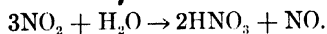
When oxygen is present also, then the NO gives more NO_2, and this in turn gives more nitric acid. This action plays an im-
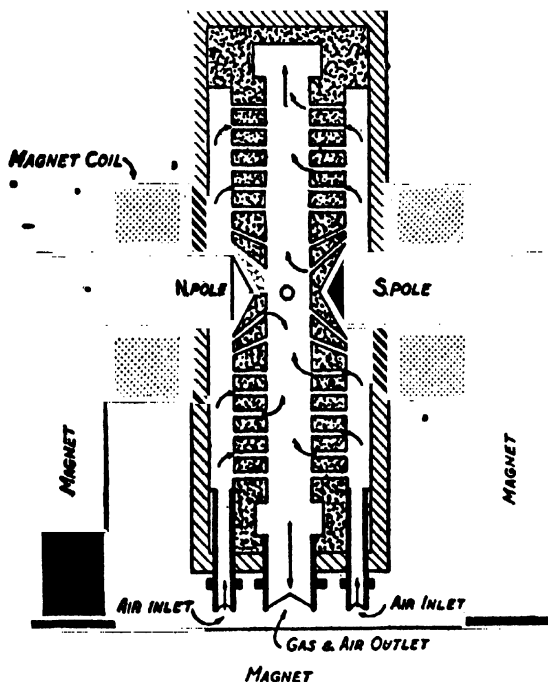
FIG. 98.

portant part in the making of nitric acid from the nitrogen of the air (see next section).

Fixation of Atmospheric Nitrogen. — Oxygen and nitrogen have no natural tendency to combine at the ordinary tempera-ture, but rather the reverse — their compounds tend to decompose

with evolution of heat. But a high temperature will supply the necessary energy. Even so, however, the union extends to only 1 per cent of the mixture at 2000° and 5 per cent at 3000°:

$$N_2 + O_2 + 43,200 \text{ calories} \rightleftarrows 2NO.$$

Note that, since the formation of NO is an endothermic reaction, the yield of NO is *increased* by raising the temperature (Van't Hoff's law, p. 216). In spite of the poor yield obtainable under the best conditions, the supply of natural nitrates is so limited that machinery has been devised, and is now in successful use, for carrying on the combination on a commercial scale. Three devices are in use, and all employ hydro-electric power.

In the **Birkeland-Eyde process** (Fig. 98), used at Notodden and elsewhere in Norway, an arc discharge between rods of carbon is spread, by the influence of powerful electromagnets, into a circular brush discharge several feet in diameter. The figure shows a cross section of the space filled by the discharge. In the center is a section of one of the carbon rods. Air is blown through the flame, giving a mixture of gases containing about 1 per cent of NO, and this is quickly cooled to permit of union of the nitric oxide with oxygen, to give the tetroxide, NO_2. The air containing NO_2 is then passed through absorbing towers down which water trickles. Here the action mentioned in the last section takes place, and an aqueous solution of nitric acid is produced. In peace times, the nitric acid is mixed with calcium hydroxide (slaked lime):

$$Ca(OH)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_2O$$
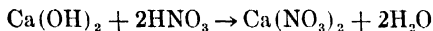
to give calcium nitrate, which, being very soluble, is sold for use as a fertilizer. In war times, the acid is concentrated for use in the manufacture of explosives.

, The **Schönherr process**, used in the same factories in Norway, employs a discharge through a tube 22 feet long (Fig. 99). The column of air rotates as it traverses the tube and so every part is exposed to the discharge.

The **Pauling process**, used in Italy and Austria, uses pre= heated air, and a different arrangement of the discharge. The principles employed are, however, the same.

The productive capacity of plants employing these arc processes in 1920 was three hundred thousand tons (calculated as nitrate of lime).

Nitric Acid from Ammonia. — The *ammonia oxidation* process for the production of nitric acid was developed on a large scale during the Great War, particularly in Germany. Gaseous ammonia in the presence of air and a suitable catalyst undergoes oxidation, with the formation of oxides of nitrogen and water vapor. The oxides of nitrogen can be recovered by absorption in water, yielding dilute nitric acid. This can be concentrated further if desired, or neutralized with a base for the production of nitrates for use as explosives (ammonium nitrate) or fertilizers (calcium nitrate).

Platinum gauze is almost universally employed as a catalyst. A mixture of ammonia and oxygen-enriched air passes through one or more layers of the gauze, which is heated electrically to 650–700° to start the reaction and which is maintained at that temperature subsequently by the heat of combustion of the ammonia. The reaction that takes place may be represented by the equation:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O.$$
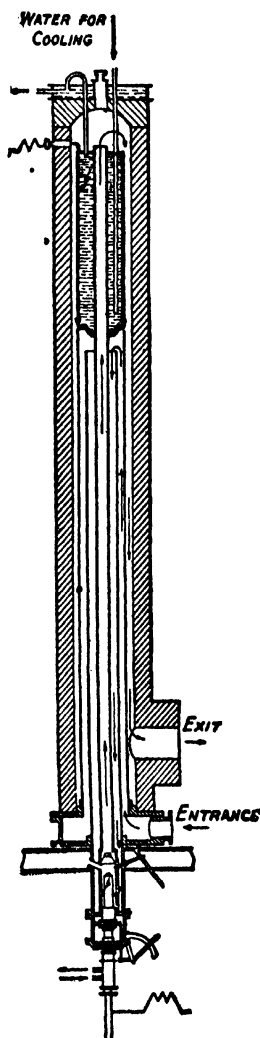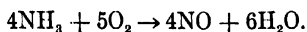
FIG. 99.

The excess oxygen present converts the NO into NO_2 as the issuing gases cool. Unless the reaction is very nicely regulated, however, the yield of oxides of nitrogen is diminished either by incomplete combustion of ammonia, or by the dissociation of NO into nitrogen and oxygen (see p. 394). The time of contact with the catalyst must not be too long, or this latter effect will be appreciable. With proper precautions, a conversion efficiency of 90–95 per cent is obtained. *Poisoning of the catalyst* must be guarded against by careful purification of the gases, especially from non-volatile impurities such as dust particles, which choke the surface of the gauze and render it inoperative.

Oxidizing Actions of Nitric Acid

When nitric acid gives up oxygen to any substance, it is itself reduced. Hence, according to convenience, we shall refer to oxidations by, or reductions of, nitric acid.

Oxidation of Hydrogen. — The metals preceding hydrogen in the electromotive series (p. 240) displace hydrogen ion from nitric acid in aqueous solution, as they do from other acids. With metals more active than zinc, such as magnesium, a great part of the hydrogen escapes in the free condition. But, in the case of zinc and the metals below it, most or all of the hydrogen is oxidized to water by the nitric acid, and part of the acid is reduced. Thus, with zinc and *very dilute* nitric acid, almost the only product, aside from zinc nitrate, is ammonia. This interacts with the excess of nitric acid present to form ammonium nitrate:

$$4Zn + 10HNO_3 \rightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

The student will find it very instructive to derive this balanced equation from its skeleton: $Zn + HNO_3 \rightarrow Zn(NO_3)_2 + NH_4NO_3 + H_2O$, using the valence method described on p. 301. Simpler, and of still greater value for the complete understanding of this and similar reactions presented immediately below, is the balancing of the equation by the use of ions and electrons, as discussed on p. 303.

Heavy Metals. — The less active metals, such as copper and silver, do not displace hydrogen from dilute acids (p. 64), but reduce nitric acid, nevertheless, and are converted into nitrates. Platinum and gold (compare p. 346) alone are not attacked. Thus copper, with somewhat *diluted* nitric acid (sp. gr. 1.2), gives cupric nitrate and nitric oxide NO:

$$8HNO_3 + 3Cu \rightarrow 4H_2O + 2NO + 3Cu(NO_3)_2.$$
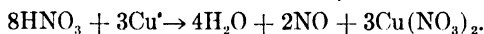
The nitric oxide is liberated as a colorless gas, but forms the brown tetroxide at once on meeting the oxygen of the air (p. 391).

When *concentrated* nitric acid is used with copper, almost pure nitrogen tetroxide is obtained:

$$4HNO_3 + Cu \rightarrow 2H_2O + 2NO_2 + Cu(NO_3)_2.$$
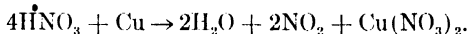
The reader should note the constant production of **nitric oxide with diluted nitric acid**, and the invariable formation of **nitrogen tetroxide with concentrated acid.** This is explained by the fact that nitrogen tetroxide cannot pass unchanged through a liquid containing much water, for it gives nitric acid and nitric oxide with the latter (p. 393). Conversely, where the nitric acid is concentrated, nitric oxide, even if formed by the interaction with the metal, must be oxidized to nitrogen tetroxide as it passes up through the liquid (p. 391).

Oxidation of Non-Metals. — With non-metals the actions are different, in so far that these elements form no nitrates. Thus sulphur boiled in nitric acid gives sulphuric acid, along with nitric oxide, equation (1), or with nitrogen tetroxide, equation (2), or with both, according to the concentration of the acid (see above):

$$2HNO_3 + S \rightarrow 2NO + H_2SO_4. \tag{1}$$
$$6HNO_3 + S \rightarrow 6NO_2 + 2H_2O + H_2SO_4. \tag{2}$$
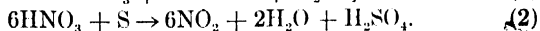
The reader will note that a separate equation, (1) and (2), must be made for the formation of *each* reduction product. If NO and NO_2 are both formed, they cannot arise from the same molecule of nitric acid. They result from two actions which are inde-

pendent, although proceeding concurrently in the same vessel (see p. 312). Thus the equation: $2HNO_3 + C \rightarrow H_2O + CO_2 + NO + NO_2$, is a misrepresentation. It implies that equimolecular quantities of the two oxides of nitrogen are formed. But this could occur only by chance, and the balance would be destroyed the next moment by the lowering in the concentration of the acid, giving the advantage to the nitric oxide.

Oxidation of Compounds: Aqua Regia. — Compounds like hydrogen sulphide and sulphurous acid, which are easily oxidized, interact with nitric acid. With diluted nitric acid, the products are free sulphur and sulphuric acid respectively.

Hydrochloric acid, which is not affected by oxidizing agents such as hydrogen peroxide or concentrated sulphuric acid, is oxidized by concentrated nitric acid. The mixture of nitric acid and hydrochloric acid is known as *aqua regia*. Chlorine is set free by the oxidation of the hydrochloric acid,

$$HNO_3 + 3HCl \rightarrow 2H_2O + Cl_2 + NOCl,$$

and nitrosyl chloride NOCl is also formed. The liquid thus contains several oxidizing agents, nitric acid, hypochlorous acid (from $Cl_2 + H_2O$), and some nitrous acid from the hydrolysis of the nitrosyl chloride. It is frequently used in analysis, for example to oxidize sulphur (say, in cast iron or in minerals), the sulphuric acid formed being estimated by precipitation and weighing of barium sulphate (p. 346).

Aqua regia (Latin, *royal water*) received its name because it converts the "noble" metals, gold and platinum, into soluble compounds. This it does because the free chlorine, in presence of hydrochloric acid, combines to form the exceedingly stable complex ions (see pp. 606-608) $AuCl_4^-$ (see chlorauric acid), and $PtCl_6^=$, the negative ion of chloroplatinic acid:

$$Pt + 2Cl_2 + 2Cl^- \rightarrow PtCl_6^=.$$

NITROUS ACID, HYPONITROUS ACID, AND THEIR ANHYDRIDES

Nitrites and Nitrous Acid. — When the nitrates of potassium and sodium are heated, they lose one unit of oxygen, and the **nitrites** remain:

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2.$$
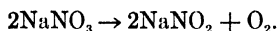
Commonly lead is stirred with the melted nitrate and assists in the removal of the oxygen. The litharge PbO which is formed remains as a residue when the sodium nitrite is dissolved for recrystallization.

When an acid is added to a *dilute* solution of a nitrite, a pale-blue solution containing **nitrous acid** HNO_2 is obtained. The acid is very unstable, however, and, when the solution is warmed, it decomposes:

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O.$$
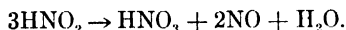
When a *concentrated* solution of sodium nitrite is acidified, the nitrous acid formed decomposes at once, and a brown gas containing the anhydride escapes:

$$2H^+ + 2NO_2^- \leftrightarrows 2HNO_2 \leftrightarrows H_2O + N_2O_3 \uparrow.$$

This behavior distinguishes a nitrite from a nitrate.

Nitrous acid is an active oxidizing agent:

$$2HI + 2HNO_2 \rightarrow 2H_2O + 2NO + I_2.$$
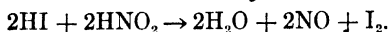
Indigo is also converted by it into isatin (compare p. 289).

Nitrous acid is much used in the making of organic dyes.

Nitrous Anhydride N_2O_3. — A study of the density of the gas arising from the decomposition of nitrous acid shows that, in the gaseous state, the anhydride is almost entirely dissociated:

$$N_2O_3 \rightleftarrows NO + NO_2.$$

When the mixture is led through a U-tube immersed in a freezing mixture at $-21°$, a deep-blue liquid is obtained which is the anhydride itself. This dissociates rapidly when allowed to boil.

The same equimolecular mixture of the two gases is obtained by the action of water on nitrosylsulphuric acid (p. 340).

Hyponitrous Acid and Nitrous Oxide N_2O. — Hyponitrous acid $H_2N_2O_2$ is a white solid. Its solution in water is an exceed-

ingly feeble acid. The warm aqueous solution decomposes slowly, giving nitrous oxide:

$$H_2N_2O_2 \rightarrow H_2O + N_2O.$$
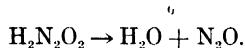
Nitrous oxide is prepared by gently heating ammonium nitrate (great care should be taken; see next page), or a solution of a salt of ammonium and a nitrate:

$$NH_4^+ + NO_3^- \rightleftarrows NH_4NO_3 \rightarrow 2H_2O + N_2O.$$
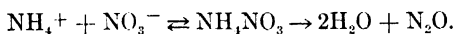
The steam condenses, and the nitrous oxide may be collected over warm water, or be dried and compressed into steel cylinders.

Its solubility in cold water is considerable: at $0°$, 130 volumes in 100; at $25°$, 60 in 100. The liquefied gas boils at $-89.8°$ and its vapor tension at $20°$ is 49.4 atmospheres.

A glowing splinter of wood bursts into flame in nitrous oxide, and phosphorus and sulphur burn in it with much the same vigor as in oxygen. In all cases oxides are formed, and nitrogen is set free. It does not combine with nitric oxide, however, as does oxygen (p. 391).

Metals do not rust in nitrous oxide, and the hæmoglobin of the blood is unable to use it as a source of oxygen. It is employed as an anæsthetic for minor operations. The hysterical symptoms which accompany its use caused it to receive the name of "laughing gas."

Graphic Formulæ of Nitric Acid and its Derivatives: Explosives. — The following equation for the formation of ammonium nitrate by neutralization of ammonium hydroxide with nitric acid shows the graphic (p. 350) formulæ of these substances:

$$\begin{matrix} H \\ H \\ H \\ H \end{matrix} N - OH + H - O - N \overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}} \rightarrow \begin{matrix} H \\ H \\ H \\ H \end{matrix} N - O - N \overset{\displaystyle O}{\underset{\displaystyle O}{\diagup}} + H_2O.$$
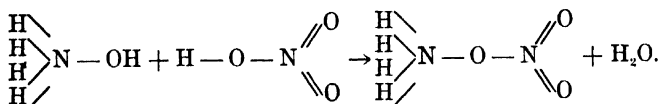
The structural formula of the nitrate is intended to explain the fact that the salt is able to exist at all, by representing the oxygen and hydrogen as being separated from one another and attached to different nitrogen units. When the equilibrium of

the system is disturbed by heating, the oxygen and hydrogen unite to form water, an arrangement which is much more stable, and nitrous oxide (p. 400) escapes with the steam. The behavior of ammonium nitrite on heating (p. 367) is explained in the same way.

It may be noted that the reaction $NH_4NO_3 \rightarrow 2H_2O + N_2O$ is accompanied by the evolution of 9000 calories of heat. This is not an excessively exothermic reaction, but if care is not taken a serious explosion is liable to result when ammonium nitrate is heated, for the compound N_2O itself decomposes into its elements at higher temperatures, and the reaction $2N_2O \rightarrow 2N_2 + O_2$ evolves an additional 38,000 calories. The final products of the decomposition of ammonium nitrate are therefore nitrogen, oxygen and water vapor, and if the decomposition is brought about suddenly these three substances, as gases, will occupy at the high temperature to which they are raised by the heat of the above reactions a volume out of all proportion to the small quantity of solid substance from which they were produced.

It is these same two factors — the endothermal character of the compounds, and their ready decomposition into simpler gaseous substances — that render many organic derivatives of nitric acid both useful and terrible as explosives (see Chapter XLII).

Exercises. — 1. Make the equation for the interaction of ferrous chloride, hydrochloric acid, and nitric acid (p. 391), and for all the actions concerned when the test for a nitrate (p. 392) is applied to sodium nitrate. What volume (at 0° and 760 mm.) of NO is obtained from one formula-weight of nitric acid?

2. In the action of zinc on dilute nitric acid (p. 396), why is not the ammonia given off as a gas? How should you show that it was formed at all?

3. Make equations for the formation of nitric oxide and nitrogen tetroxide by the action of carbon on nitric acid (p. 397).

4. Make equations for the interaction of iron with diluted and with concentrated nitric acid, respectively (p. 397). The iron gives ferric nitrate $Fe(NO_3)_3$.

5. Give the three ways in which nitrates decompose when heated, with one equation illustrating each.

6. Make all the equations for oxidations on pp. 396-398, using the methods illustrated on pp. 301-305.

7. How could you distinguish nitric oxide, (a) from hydrogen, (b) from oxygen?

CHAPTER XXVIII

The Chemical Relations of the Element. — There are many things in the chemistry of phosphorus and its compounds which remind us of nitrogen. Yet these are largely referable to the fact that the elements are both non-metals and both have the same main valences, viz., three and five. The behavior of the compounds is often very different. For the present it is sufficient to say that both give compounds with hydrogen, NH_3 and PH_3, and both yield oxides of the forms X_2O_3, X_2O_4, and X_2O_5. The first and last of these oxides are acid-forming, and phosphorus, therefore, gives acids corresponding to nitrous and nitric acids. The element is thus a non-metal.

Occurrence. — Calcium phosphate $Ca_3(PO_4)_2$ forms about 25 to 27 per cent of the material of the bones and teeth of animals. The same salt occurs in deposits, as a mineral, and is found scattered through all fertile soils. Complex organic compounds of phosphorus, such as lecithin, are essential constituents of the muscles, nerves and brains of animals and are found also in plants. The average man's skeleton contains 1400 g. of phosphorus, his muscles 130 g., and his nerves and brain 12 g. Amongst foods, egg-yolks and beans contain an unusually large proportion, nuts, peas, and wheat (entire grain) coming next.

Phosphorus was discovered by Brand in 1669, and by Kunkel in 1670, by distilling at a white heat the solid residue from evaporated animal matter. They were both searching for the philosophers' stone. Scheele in Sweden prepared it from bones in 1771. The element is used chiefly in the manufacture of matches.

Manufacture of Phosphorus. — Phosphorus is now manufactured by mixing natural calcium phosphate with the proper

proportions of carbon and silicon dioxide (sand), and the mixture is introduced continuously into an electric furnace (Fig. 100), entering at the top B through a worm feed A. The discharge of an alternating current between carbon poles C and C produces the very high temperature which the action requires.
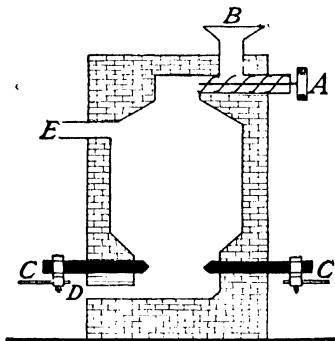
The calcium silicate which is formed fuses to a slag, and can be withdrawn at intervals through a pipe D at the bottom of the furnace. The gaseous products distil off through a pipe E and the phosphorus is condensed by means of cold water:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow$$
$$3CaSiO_3 + 5CO + 2P.$$

FIG. 100.
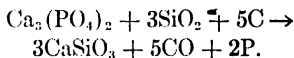
We may regard the phosphate as being composed of two oxides, $3CaO,P_2O_5$. It thus appears that the calcium oxide has united with the silica, which is an acid anhydride (see p. 311): $CaO + SiO_2 \rightarrow CaSiO_3$, while the phosphoric anhydride has been reduced.

The phosphorus, after purification, is cast into sticks in tubes of tin or glass, standing in cold water.

Physical Properties. — There are at least two allotropic forms (p. 290) of phosphorus, known as white phosphorus and red phosphorus. **White phosphorus,** prepared as described above, is at first transparent and colorless, but after exposure to light acquires a superficial coating of the red variety. It melts at 44° and boils at 287°. Its sp. gr. is 1.83. Its molecular weight at 313° is 128 and the formula, therefore, P_4 (see p. 122). White phosphorus is soluble in carbon bisulphide, less soluble in ether, and insoluble in water. It is exceedingly poisonous, less than 0.15 g. being a fatal dose, and is an ingredient in roach-paste and rat poison. Continued exposure to its vapor causes necrosis, a disease from which match-makers are liable to suffer. The jawbones and teeth are particularly liable to attack.

Red phosphorus is a red powder consisting of small tabular crystals. It is obtained by heating white phosphorus to about 250° in a vessel from which air is excluded. Much heat is evolved in the transformation. Red phosphorus does not melt, but passes directly into vapor, identical with that of white phosphorus. It is insoluble in carbon bisulphide and other solvents. It is not poisonous, and, unlike white phosphorus, does not require to be kept under water to avoid spontaneous combustion. Red phosphorus appears to be a solid solution (p. 139) of the white variety in a less active kind. Hence, its properties are variable, *e.g.*, sp. gr. from 2.05 to 2.34. Bridgman, by heating white phosphorus at 200° under a pressure of 1200 kg. per sq. cm., has obtained **black phosphorus** (sp. gr. 2.69) which may be the pure form of the red variety.

Chemical Properties. — White phosphorus unites directly with the halogens with great vigor. It unites slowly with oxygen in the cold, and with sulphur and many metals when the materials are heated together. The slow union of *cold* phosphorus with atmospheric oxygen is accompanied by the evolution of light. Hence the word phosphorescence. The name of the element (Greek $\phi \tilde{\omega}s$, light; $\phi \acute{\epsilon} \rho \omega$, I bear) records this property. Apparently the chemical energy, transformed in connection with the oxidation, is converted, in part at least, into radiant energy instead of completely into heat.* The slow oxidation of phosphorus is accompanied by the production of ozone, but the nature of the action is still unknown (see p. 287).

When phosphorus burns in *perfectly dry* air, the cloud of solid pentoxide particles very quickly subsides. When phosphorus burns in *moist* air, however, the cloud of pentoxide forms tiny droplets, consisting of a concentrated solution of phosphoric acid, which remain suspended in the atmosphere as a *fog* (compare sulphur trioxide, p. 338). Burning phosphorus was therefore used in the war for screening the movement of vessels. In land warfare, shells containing white phosphorus were also employed for

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* The same production of light from chemical action in a cold body is seen in the luminosity of certain parts of fireflies and some species of fish.

incendiary purposes. Such shells produced horrible; and usually fatal, burns on any enemy within the radius of their explosion.

Red phosphorus, since it is formed with evolution of heat, contains less energy than white phosphorus and is much less active. It does not catch fire below 240°, while ordinary phosphorus ignites at 35°.

Manufacture of Matches. — These are of two kinds, ordinary matches, which strike on any rough surface, and "safety" matches. Ordinary matches are still made in some countries by dipping the splints of wood in melted paraffin, and then in a paste made of 4 to 7 per cent of white phosphorus, lead dioxide about 50 per cent, water, and dextrin (paste). The head, when dry, is dipped in varnish to exclude air and moisture. Where the use of white phosphorus is very properly forbidden, a sulphide P_4S_3 is substituted. When the match is struck, the friction explodes the mixture of phosphorus trisulphide (combustible) and lead dioxide (or other oxidizing agent), and the resulting heat sets fire to the paraffin and this, in turn, to the wood.

Safety matches carry no phosphorus, but only a mixture of substances containing oxygen, such as potassium chlorate or potassium chromate, with a combustible, like antimony trisulphide, some dextrin and a filling (*e.g.*, chalk). The box is coated with a mixture of red phosphorus, antimony trisulphide, dextrin and filling. The friction converts a trace of the red phosphorus into the white variety, and the latter sets fire to the head.

Phosphine. — Three hydrides of phosphorus are known. These are, phosphine PH_3 (a gas), a liquid hydride P_2H_4, which is presumably the analogue of hydrazine (N_2H_4), and a solid hydride P_4H_2.

Phosphine PH_3 is readily prepared by boiling white phosphorus with potassium hydroxide solution in a flask provided with a delivery tube (Fig. 101). Potassium hypophosphite is formed at the same time:

$$3KOH + 4P + 3H_2O \rightarrow 3KH_2PO_2 + PH_3 \uparrow.$$
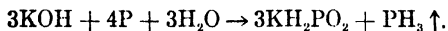
The gas made in this way contains a little of the vapor of the liquid hydride, which is spontaneously inflammable, and conse-

quently the bubbles of the mixture catch fire when they reach the surface of water in the trough: $PH_3 + 2O_2 \rightarrow H_3PO_4$. In still, moist air, the fog of droplets of phosphoric acid solution form beautiful smoke rings. It is advisable to pass a current
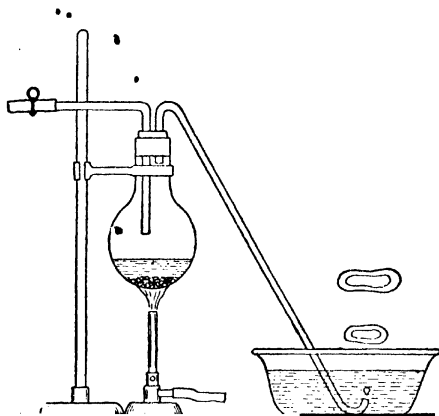
FIG. 101.

of illuminating gas, nitrogen or some other inert gas through the flask by means of a second glass tube (afterwards closed with a clip, see Fig. 101) for a few minutes before starting to heat, in order to displace all the oxygen inside the flask.

The simplest method of preparing phosphine is by the action of water upon calcium phosphide:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3.$$
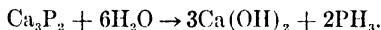
This action is analogous to that of water upon magnesium nitride (p. 383), by which ammonia is produced.

Phosphine is a colorless gas, which is easily decomposed by heat into its elements. It is exceedingly poisonous and, unlike ammonia, it is insoluble in water, and furnishes no basic compound corresponding to ammonium hydroxide. It resembles ammonia, formally at least, in uniting with the hydrogen halides (see below). It differs from ammonia, however, inasmuch as it

does, not unite with the oxygen acids. Phosphine acts upon solutions of some salts, precipitating phosphides of the metals:

$$3CuSO_4 + 2PH_3 \rightarrow Cu_3P_2 \downarrow + 3H_2SO_4.$$
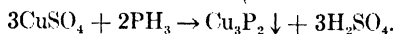
Shells containing metallic phosphides are of service in naval warfare as *markers* in night engagements, the impure phosphine produced by the action of the water on the phosphides burning spontaneously on the surface and indicating the position of the shot.

Phosphonium Compounds. — Hydrogen iodide unites with phosphine to form a colorless solid, crystallizing in beautiful, highly refracting, square prisms: $PH_3 + HI \rightarrow PH_4I$. Hydrogen chloride combines similarly with phosphine, but only when the gases are cooled by a freezing mixture, or are brought together under a total pressure of 18 atmospheres at 14°. When the pressure is released, rapid dissociation occurs.

In imitation of the ammonia nomenclature, these substances are called **phosphonium iodide** and phosphonium chloride PH_4Cl. They are entirely different, however, from the corresponding ammonium derivatives, for the PH_4^+ ion is unstable. When brought in contact with water they decompose into their constituents, the hydrogen halide going into solution, and the phosphine being liberated as a gas.

Halides of Phosphorus. — The existence of the following halides has been proved conclusively:

. . . .	. . . .	. . . .	P_2I_4 (solid)
PF_3 (gas)	PCl_3 (liquid)	PBr_3 (liquid)	PI_3 (solid)
PF_5 (gas)	PCl_5 (solid)	PBr_5 (solid)	. . . .

These substances may all be formed by direct union of the elements. They are incomparably more stable than are the similar compounds of nitrogen. They are all hydrolyzed by water, and give an oxygen acid of phosphorus and the hydrogen halide (see below). This action was used in the preparation of hydrogen bromide (p. 273) and hydrogen iodide (p. 278).

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Phosphorus trichloride PCl_3 is made by passing chlorine gas over melted phosphorus in a flask until the proper gain in weight has occurred. The substance, a liquid boiling at 76°, is stable (see p. 43). When excess of chlorine is employed, **phosphorus pentachloride** PCl_5, a white solid body, is formed. When moist air is blown over any of these substances, the water is condensed to a fog by the hydrogen halide. In the case of the interaction of the pentachloride and water, phosphoric acid is formed:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl.$$
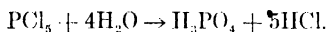
Phosphorus pentachloride, when heated under ordinary atmospheric pressure, *sublimes* (see p. 276) at 163°. When heated in a sealed tube under increased pressure it melts at 166°. In the saturated vapor at the subliming point, about 4 per cent of the molecules are dissociated into phosphorus trichloride and chlorine (p. 122): $PCl_5 \rightleftarrows PCl_3 + Cl_2$.

Oxides of Phosphorus. — The oxides of phosphorus are the trioxide P_2O_3 or P_4O_6, the pentoxide P_2O_5, and a tetroxide P_2O_4.

The **pentoxide** is a white powder formed when phosphorus is burned with a free supply of oxygen. It unites with water with great violence to form, finally, phosphoric acid (see below), and hence is known as **phosphoric anhydride.** In the laboratory this action is frequently utilized for drying gases (p. 369) and for removing water from combination (p. 390). The vapor density leads to the formula P_4O_{10}, use of which, however, would only complicate our equations in reactions in which the vapor state is not concerned.

The **trioxide** is obtained by burning phosphorus in a tube with a restricted supply of air. It is a white solid, melting at 22.5° and boiling at 173°. This oxide is the anhydride of phosphorous acid, but it unites exceedingly slowly with cold water to form this substance. When its vapor is heated to 440° it decomposes, giving the **tetroxide** P_2O_4 and red phosphorus.

Acids of Phosphorus. — There are six different acids of phosphorus. *Three* are phosphoric acids, representing the same stage

of oxidation of phosphorus, but different degrees of hydration of the anhydride. The others show three different and lower states of oxidation (study by positive and negative valences, p. 301):

Orthophosphoric acid	H_3PO_4 ($= 3H_2O,P_2O_6$)
Pyrophosphoric acid	$H_4P_2O_7$ ($= 2H_2O,P_2O_6$)
Metaphosphoric acid	HPO_3 ($= H_2O,P_2O_6$)
Hypophosphoric acid	H_2PO_3 ($= 2H_2O,P_2O_4$)
Phosphorous acid	H_3PO_3 ($= 3H_2O,P_2O_3$)
Hypophosphorous acid	H_3PO_2 '($= 3H_2O,P_2O$)

The Phosphoric Acids. — The relation between the three different phosphoric acids may be seen by considering them as being formed from phosphorus pentoxide (the anhydride) and water. In the majority of cases already considered this sort of action takes place in but one way. Thus, nitric acid is known in but one form, which is produced by the union of one molecule each of nitrogen pentoxide and water: $N_2O_5 + H_2O \rightarrow 2HNO_3$. Similarly, the chief sulphuric acid is the one formed from one molecule of sulphur trioxide and one molecule of water: $SO_3 + H_2O \rightarrow H_2SO_4$, although here we have also pyrosulphuric (fuming sulphuric) acid $H_2S_2O_7$, or $H_2O,2SO_3$.

Now, when phosphoric anhydride acts upon water we obtain a solution which, on immediate evaporation, leaves a glassy solid, HPO_3, known as **metaphosphoric acid.** When, however, the solution is allowed to stand for some days, or is boiled with a little dilute nitric acid, whose hydrogen-ion acts catalytically, the residue from evaporation is H_3PO_4, **orthophosphoric acid** (ordinarily called just **phosphoric acid**):

$$HPO_3 + H_2O \rightarrow H_3PO_4.$$
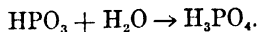
Conversely, when orthophosphoric acid is kept at about 255° for a time, it slowly loses water, and $H_4P_2O_7$, **pyrophosphoric acid,** is obtained:

$$2H_3PO_4 \rightarrow H_2O + H_4P_2O_7.$$
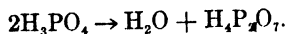
Further desiccation leaves metaphosphoric acid. When dissolved in water, pyrophosphoric acid slowly resumes the water

which it has lost and gives the ortho-acid again. The relations of all these substances are more clearly seen in the graphic formulæ:

$$P \begin{cases} = O \\ -O-H \cdot \\ -O-H \\ -O-H \end{cases} \quad P \begin{cases} = O \\ -O-H \\ -O-H \end{cases} \quad P \begin{cases} = O \\ -O-H \\ = O \end{cases} \quad P \begin{cases} = O \\ = O \end{cases}$$

$$+ \qquad \rightarrow \qquad \begin{cases} = O \\ -O-H \end{cases} \rightarrow + \cdot \qquad \rightarrow P \begin{cases} = O \\ = O \\ = O \end{cases} \cdot$$

$$P \begin{cases} -O-H \\ -O-H \\ -O-H \\ = O \end{cases} \quad P \begin{cases} -O-H \\ = O \end{cases} \quad P \begin{cases} = O \\ -O-H \\ = O \end{cases}$$

$$+ H_2O \qquad + 2H_2O \qquad + 3H_2O$$
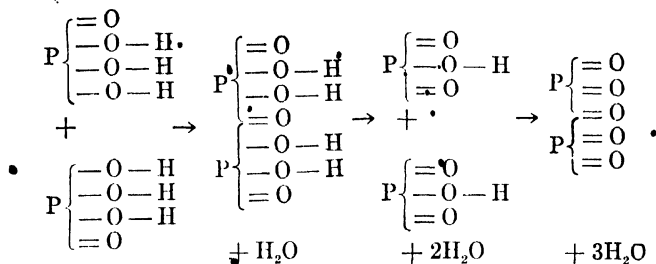
A most important fact to be noted is that the *addition or removal of water leaves the valence of the phosphorus unchanged.* The degree of oxidation of the phosphorus and its valence are *identical* in the three acids.

Orthophosphoric Acid H_3PO_4. — The impure, commercial acid is made by mixing selected, pulverized phosphate rock $Ca_3(PO_4)_2$ with sulphuric acid (sp. gr. 1.5) and heating with steam and stirring in a wooden vat:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \leftrightarrows 2H_3PO_4 + 3CaSO_4 \downarrow.$$
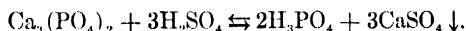
The calcium sulphate is precipitated during the heating and the subsequent concentration of the filtrate.

Pure orthophosphoric acid may be made by boiling red phosphorus with slightly diluted nitric acid and evaporating the water and excess of nitric acid.

The acid is a typical transition acid (see table on p. 244), and is dissociated chiefly into the ions H^+ and $H_2PO_4^-$. The further dissociation of the latter ion into H^+ and $HPO_4^=$ takes place to only a very small extent. The ion $HPO_4^=$ also possesses only a very slight tendency to break up into H^+ and $PO_4^{\equiv}$. The concentration of these last-mentioned ions in an acid solution is therefore negligible.

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \rightleftarrows H^+ + HPO_4^= \rightleftarrows H^+ + PO_4^{\equiv}$$
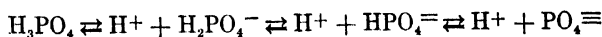
Salts of Orthophosphoric Acid. — As a **tribasic acid**, it forms salts of three kinds, such as NaH_2PO_4, Na_2HPO_4, and Na_3PO_4. These are known respectively as **primary, secondary,** and **tertiary** sodium orthophosphate. The primary sodium phosphate is faintly acid in reaction (compare sodium bisulphite, p. 335). The secondary one is slightly 'alkaline, because of hydrolysis (compare acid sodium sulphide, p. 325). The tertiary phosphate is stable only in solid form (compare normal sodium sulphide, p. 324), and can be made by evaporating to dryness a mixture of the secondary phosphate and sodium hydroxide:

$$Na_2HPO_4 + NaOH \rightleftarrows Na_3PO_4 + H_2O \uparrow .$$
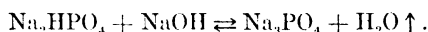
When the product is dissolved in water, this action is reversed (compare p. 327). Mixed phosphates are also known, particularly sodium-ammonium phosphate (**microcosmic salt**) $NaNH_4HPO_4$, $4H_2O$, and the insoluble magnesium-ammonium phosphate $MgNH_4PO_4$. Primary calcium phosphate (see p. 527), known in commerce as "super-phosphate," is used as a fertilizer.

The tertiary **phosphates** are unchanged by **heating.** The primary and secondary phosphates, however, retaining, as they do, some of the original hydrogen of the phosphoric acid, are capable of losing water, like phosphoric acid itself, when heated. The actions are slowly reversed when the products are dissolved in water:

$$NaH_2PO_4 \rightleftarrows NaPO_3 + H_2O \uparrow .$$
$$2Na_2HPO_4 \rightleftarrows Na_4P_2O_7 + H_2O \uparrow .$$
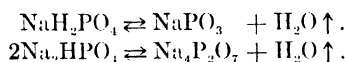
It will be seen that the **meta-** and **pyrophosphates of sodium** are formed by these actions; and this is indeed the simplest way of forming these substances, since the acids themselves are not permanent in solution, and are too feeble to lend themselves to exact neutralization. Ammonium salts of phosphoric acid lose ammonia, as well as water, when heated (see p. 386). Thus, microcosmic salt gives primary sodium phosphate:

$$NaNH_4HPO_4 \rightarrow NH_3 \uparrow + NaH_2PO_4 \rightarrow NaPO_3 + H_2O \uparrow ,$$
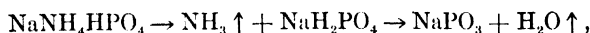
and this in turn is converted into the metaphosphate by loss of water.

Pyrophosphoric Acid and Metaphosphoric Acid. — **Pyro-phosphoric acid** $H_4P_2O_7$, although tetrabasic, gives only the normal salts, such as $Na_4P_2O_7$, and those in which one-half of the hydrogen has been displaced by a metal, such as $Na_2H_2P_2O_7$.

Metaphosphoric acid HPO_3 is the "glacial phosphoric acid" of commerce, and is usually sold in the form of transparent sticks. It is obtained by heating orthophosphoric acid, or by direct union of phosphorus pentoxide with a small amount of cold water. It passes into vapor at a high temperature, and its vapor density corresponds to the formula $(HPO_3)_2$.

Sodium metaphosphate $NaPO_3$, in the form of a small globule obtained by heating microcosmic salt on a platinum wire, is used in analysis. When minute traces of oxides of certain metals are placed upon such a globule, known as a **bead,** and heated in the Bunsen flame, the mass is colored in various tints according to the oxide used (**bead test**). This action may be understood when we consider that sodium metaphosphate takes up water to form primary sodium orthophosphate: $NaPO_3 + H_2O \rightarrow NaH_2PO_4$. In the same way, but at higher temperatures, it is able to take up oxides of elements other than hydrogen, giving mixed ortho-phosphates. Thus, with oxide of cobalt a part of the metaphosphate unites according to the equation:

$$NaPO_3 + CoO \rightarrow NaCoPO_4,$$
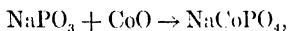
and the product gives a blue color to the bead.

Distinguishing Tests. — When a solution of **nitrate of silver** is added to a solution of orthophosphoric acid, or to any soluble orthophosphate, a yellow precipitate of silver orthophosphate Ag_3PO_4 is produced. This is a test for orthophosphates. With pyrophosphoric acid or any pyrophosphate the product is white $Ag_4P_2O_7$. With metaphosphoric acid a white precipitate, $AgPO_3$, is obtained also. Metaphosphoric acid coagulates a clear solution (colloidal suspension) of albumen (say, white of egg), while ortho- or pyrophosphoric acid has no visible effect upon it.

Phosphorous Acid H_3PO_3. — When added to cold water, phosphorus trioxide yields phosphorous acid very slowly. This

acid may be obtained much more easily by the action of water upon phosphorus trichloride, tribromide (p. 273), or tri-iodide and evaporation of the solution: '

$$PCl_3 + 3H_2O \rightarrow P(OH)_3 + 3HCl \uparrow .$$
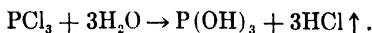
Phosphorous acid is a powerful reducing agent, precipitating silver, for example, in the metallic form from solutions of its salts. When heated, it decomposes, giving the most stable acid of phosphorus (compare pp. 314, 335), namely metaphosphoric acid, and phosphine:

$$4H_3PO_3 \rightarrow 3HPO_3 + 3H_2O + PH_3.$$
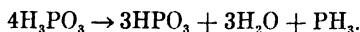
Comparison of Phosphorus with Nitrogen and with Sulphur. — Although phosphorus and nitrogen are regarded as belonging to one family, the differences between them are more conspicuous than the resemblances. The latter are confined almost wholly to matters concerned with valence. The contrasts between phosphine and ammonia (p. 407) and between the halides of the two elements (pp. 387, 408) have been noted already. The pentoxide of nitrogen decomposes spontaneously; that of phosphorus is one of the most stable of compounds. Nitric acid is very active, both as acid and oxidizing agent; the phosphoric acids are quite the reverse.

On the other hand, the resemblance of phosphorus to sulphur is marked. Both are solids, existing in several forms. Both yield stable compounds with oxygen and chlorine. The hydrogen compounds interact with salts to give phosphides of metals and sulphides of metals, respectively. Against these must be set the facts, that hydrogen sulphide does not unite with the hydrogen halides at all while phosphine gives the phosphonium halides, and that phosphoric acid is hard to reduce while sulphuric acid is reduced with comparative ease.

Exercises. — 1. What are the valences of the non-metals in: $H_2S_2O_7$, $H_2Cr_2O_7$, $KMnO_4$, KH_2PO_2, H_3PO_4, NaH_2PO_3, Na_2PO_3? Name these substances.

2. Is it oxidation or reduction, or neither, when we make, (a)

N_2O_4 from HNO_3, (b) SO_2 from H_2SO_3, (c) HPO_3 from H_3PO_3, (d) $H_2S_2O_7$ from H_2SO_4, (e) Na_2SO_4 from $NaHSO_3$?

3. Why would a mixture of potassium dichromate and hydrochloric acid (p. 323) be less suitable than nitric acid, as an oxidizing agent for making phosphoric acid from red phosphorus?

4. Why is not the tertiary phosphate of sodium (p. 412) decomposed by heating? What tertiary phosphates would be decomposed by this means?

5. Formulate the hydrolyses of the secondary and tertiary sodium orthophosphates as was done for sodium sulphide (pp. 324-325).

6. How should you prepare $Ca_2P_2O_7$ and $Ca(PO_3)_2$, both insoluble?

7. What product should you confidently expect to find (p. 410) after heating, (a) sodium phosphite, Na_2HPO_3, (b) potassium hypophosphite (p. 407)? Make the equations.

8. Compare the elements chlorine and phosphorus after the manner of the comparisons on p. 414.

CHAPTER XXIX

CARBON AND THE OXIDES OF CARBON

THE majority of the substances composing, or produced by, living organisms, such as starch, fat, and sugar, are compounds of carbon. Hence the chemistry of these compounds is known as **organic chemistry.** It was at first supposed that the artificial production of such compounds, *e.g.*, without the intervention of life, was impossible. But many natural organic products have now been made from simpler ones or from the elements, and the preparation of the others is delayed only in consequence of difficulties caused by their instability and complexity. On the other hand, hundreds of compounds unknown to animal or vegetable life, including many valuable drugs and dyes, have now been added to the catalogue of chemical compounds. Hundreds of thousands of different compounds containing carbon are known, and thousands more are added every year.

The elements entering into carbon compounds are chiefly hydrogen and oxygen. After these, nitrogen, phosphorus, the halogens and sulphur may be named.

CARBON C

Occurrence. — Large quantities of carbon are found in the free condition in nature. The **diamond** is the purest natural carbon. **Graphite,** or plumbago, which is the next purest, is found in limited amounts, and is a valuable mineral. **Coal** occurs in numerous forms containing greatly varying proportions of free carbon. Small quantities of the free element have been found in meteorites.

In combination, carbon is found in **marsh-gas, or methane** CH_4, which is the chief component of natural gas. The numerous compounds found in plants and animals have already been mentioned. The **mineral oils** consist almost entirely of mixtures of

various compounds of carbon and hydrogen (hydrocarbons). Whole geological formations are composed of *carbonates of common metals*, particularly **calcium carbonate or limestone.**

Diamond. — This allotropic modification of carbon is distinguished by its natural crystalline form, which often resembles the octahedron (Fig. 44, p. 105). The ultimate structure of the diamond crystal is represented in Fig. 50 (p. 107). Its specific gravity is **3.5.** For ornamental purposes the diamond is "cut" by grinding new faces so as to give artificial forms called "brilliants" (Fig. 102) and "rosettes." These forms are given to the stone, in order that the maximum reflection of light from its interior may be produced. It is the hardest of familiar substances, and can be scratched or polished only

Fig. 102.

by rubbing with diamond powder. The colorless stones and those with special tints are valuable. The black ("carbonado") and badly colored specimens are less valuable and are used for grinding, for glass-cutting, and on the points of drills.
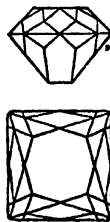
Diamonds are found chiefly in South Africa and Brazil. They are separated from the rock by weathering and washing. They are sold by the carat (1 international carat = 200 mg.) and the value increases with the size. The largest known specimen, the Cullinan, weighed 3032 carats before being cut.

Small synthetic diamonds are obtained when molten iron containing dissolved carbon is suddenly chilled. If the fused mass is allowed to cool gradually, however, the carbon separates out in the form of graphite.

Graphite. — Graphite (Greek, *I write*) is found in nature in Siberia, Cumberland, Brazil, Ceylon and elsewhere. It forms dark grey or black hexagonal tablets, and, when pulverized, it gives slippery scales of microscopic size. Unlike the diamond, it is quite soft, has a specific gravity of **2.3,** and conducts electricity. Natural graphite is usually mixed with foreign matter, and even the purest specimen leaves, when burned, from **2 to 5** per cent of ash. It is called also **plumbago, or black lead.**

Graphite, moulded into blocks, is sawn into rods for the cores of "lead" pencils (first used in the 16th century). Clay is added in varying proportions to give different degrees of hardness. Because of its infusibility, it is used to make crucibles. Smeared on a plaster cast (non-conductor), it gives a conducting surface on which metals (copper or silver) can be deposited by electrolysis. A thin layer, used as stove-polish, protects the iron from rusting. In electro-chemical industries it is used for electrodes at which chlorine is to be liberated; all other conductors interact chemically with this element and are destroyed.'
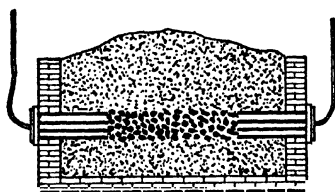
It is employed also as a lubricant, when wooden beams slide upon one another.

Large amounts of pure graphite are now manufactured by heating coke with some pitch and a little sand or ferric oxide (Acheson's process). The mixture (3 to 3½ tons) is piled (Fig. 103) between the electrodes connected with a dynamo, and, on account of its high resistance, becomes strongly heated. The operation is complete in from 24 to 30 hours.

Fɪɢ. 103.

Other Forms of Carbon. — The apparently amorphous varieties of carbon are numerous. They include **wood-charcoal, lampblack, animal charcoal, coal** (e.g., bituminous coal and anthracite) and **coke.** All of these substances will come up for discussion in later chapters. None of them, it may be noted here, is composed of pure carbon, other elements being present, mostly in combination with carbon, in very variable amounts.

Examination of "amorphous" charcoal by X-ray methods indicates that it possesses a crystalline structure identical with that of graphite. Charcoal is not to be regarded, therefore, as a supercooled liquid (see p. 106) like glass. It consists of tiny fragments of graphite. The amorphous appearance is due to the extreme minuteness of the crystals, which are interspersed, with attendant impurities, through a highly porous mass.

Chemical Properties of Carbon. — The most common uses of carbon depend upon its great tendency to unite with oxygen, forming carbon dioxide CO_2. With a limited supply of oxygen, carbon monoxide CO (see p. 426) is produced. Aside from the direct employment of these reactions for the sake of the heat which is liberated (see p. 289), they are used also in the reduction of ores of iron, copper, zinc, and many other metals. When, for example, finely powdered cupric oxide and carbon are heated, copper is obtained. The gas given off is either carbon dioxide, or a mixture of this with carbon monoxide, according to the proportion of carbon and the temperature used:

$$Cu_2O + C \rightarrow Cu + CO,$$
$$2CuO + C \rightarrow 2Cu + CO_2.$$
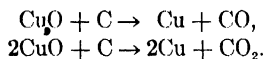
At the high temperatures produced in the electric furnace, carbon unites with many metals and some non-metals. Thus, when dissolved in molten iron, it forms iron carbide Fe_3C. Other examples will be taken up in succeeding sections.

The union with hydrogen is ordinarily too slow to be observed. But when the carbon is mixed with pulverized nickel (contact agent), and hydrogen is passed over the mixture at 300°, methane CH_4 is formed (97 per cent). The action is reversible and exothermal, and is therefore, at higher temperatures, less complete (see p. 217), at 850° reaching only 1.6 per cent. On the other hand, an electric arc, between carbon poles in an atmosphere of hydrogen, gives traces of acetylene C_2H_2, this action being endothermal. The other compounds of carbon and hydrogen are all obtained by indirect reactions.

Carbon Disulphide CS_2. — This compound is made by direct union of sulphur vapor and glowing charcoal. An electric furnace like that in Fig. 100 (p. 404) is employed. The substance comes off as a vapor and is condensed.

Carbon disulphide is a colorless, highly refracting liquid (b.-p. 46°). Traces of other compounds give the commercial article a disagreeable smell. It burns in air, forming carbon dioxide and sulphur dioxide. It is an important solvent for sulphur and caoutchouc (rubber), and dissolves iodine and

phosphorus freely. Large quantities are employed also in the destruction of prairie dogs and ants and for freeing grain elevators of rats and mice.

Carbon Tetrachloride CCl₄. — This compound is manufactured by leading dry chlorine into carbon disulphide containing a little iodine (contact agent) in solution:

$$CS_2 + 3Cl_2 \rightarrow CCl_4 + S_2Cl_2.$$
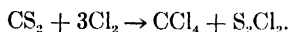
On distilling the resulting mixture, the carbon tetrachloride CCl_4 (b.-p. 77°) passes off and is condensed, while the sulphur monochloride S_2Cl_2 (b.-p. 136°) remains.

Carbon tetrachloride is a colorless liquid. It dissolves fats and tars and other organic compounds, and has the advantage over benzine and gasoline of being non-inflammable. It is therefore used in taking the grease out of wool, linen cloth, oil-bearing seeds, and bones. Many liquids sold for dry cleaning and removing stains from clothing, gloves, etc., consist of carbon tetrachloride diluted with a cheaper material, such as benzine. Although the proportion of such material originally added may be insufficient to render the mixture inflammable or explosive, the risk exists that evaporation of the more volatile carbon tetrachloride may eventually bring the composition of the residue into the dangerous region. Products containing no benzine are therefore to be preferred.

Carbides and the Electric Furnace. — Chemical actions which proceed only at very high temperatures are most economically carried out by using electricity as the source of heat. In such cases the electricity has no electrolytic or other chemical action. There are two types of electric furnaces. In the making of graphite (p. 418) and of phosphorus (p. 404), which illustrates one of them, the resistance of the carbon furnishes the occasion for the rise in temperature.

Of the same type is the furnace used for making **carborundum** (SiC, silicon carbide), manufactured in large quantities at Niagara Falls (Acheson's process). The coke and sand (silicon dioxide SiO_4) are piled between the terminals, and the resistance

of the former causes the production of the heat, as in Fig. 103, p. 418:

$$3C + SiO_2 \rightarrow SiC + 2CO \uparrow .$$
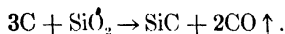
Here the carbon reduces the oxide, and combines with the element (Si) as well. The product (SiC) is exceedingly hard, and, after pulverization and mixing with other materials, is moulded into grinding wheels.

In the other type of furnace the air between the terminals furnishes the resistance, and the *arc* (a discharge carried by the badly conducting air and carbon vapor) furnishes the heat. This type of furnace is employed in various "arc processes" for the fixation of atmospheric nitrogen (p. 394).

The arc is also of assistance in the manufacture of **calcium carbide** (CaC_2), which involves the heating of a mixture of lime and coke to a very high temperature (estimated at 3000°). The reaction is carried out in large graphite crucibles, which form the negative electrodes. The positive electrodes consist of large blocks of graphite, which are gradually consumed in the passing of the arc:

$$CaO + 3C \rightarrow CO + CaC_2.$$
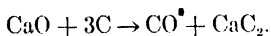
Cold water acts vigorously with calcium carbide, giving **acetylene** gas C_2H_2 (see p. 439) and calcium hydroxide (slaked lime):

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow .$$
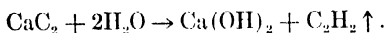
CARBON DIOXIDE AND CARBONIC ACID

Occurrence. — Carbon dioxide is present in the atmosphere, and issues from the ground in large quantities in certain neighborhoods, as, for example, in the so-called Valley of Death in Java, and in the Grotta del Cane near Naples. Effervescent mineral waters, such as those of Vichy and of the Geyser Spring at Saratoga, contain it in solution, and their effervescence is caused by the escape of the gas when the pressure is reduced.

Modes of Formation. — 1. Carbon dioxide is produced by combustion of carbon with an *excess* of oxygen: $C + O_2 \rightarrow CO_2$. The combustion of all compounds of carbon, as well as the slow

oxidation in the tissues of plants and animals, yield the same product. The product from burning carbon is naturally mixed with at least four times its volume of atmospheric nitrogen. To secure carbon dioxide for commercial purposes from this source, the gas is led under pressure into a solution of potassium carbonate, which absorbs the carbon dioxide:

$$CO_2 \text{ (gas)} \rightleftarrows CO_2 \text{(dslvd)} + H_2O \rightleftarrows H_2CO_3 + K_2CO_3 \rightleftarrows 2KHCO_3.$$
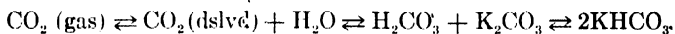
When the pressure is reduced by a pump, all the actions are reversed, and the gas escapes in pure form. The same solution, with occasional purification, can be used an indefinite number of times.

2. It was Joseph Black (1757) who first recognized the gas as a distinct substance. He observed its formation when marble or chalk was heated:

$$CaCO_3 \rightleftarrows CaO + CO_2,$$

and named the gas "fixed air" from the fact that it was contained in these solids. The above action had been used for centuries in making quicklime (calcium oxide). All common carbonates, excepting those of potassium and sodium, decompose when heated, the oxide of the metal or the metal itself remaining.

3. Black found that the gas was also produced when acids acted upon carbonates, and this is the method employed in the laboratory:

$$\left.\begin{array}{l} CaCO_3\text{(solid)} \rightleftarrows CaCO_3\text{(dissolved)} \rightleftarrows Ca^{++} + CO_3^{=} \\ 2HCl \text{ (dissolved)} \rightleftarrows 2Cl^- + 2H^+ \end{array}\right\} \rightleftarrows H_2CO_3 \rightleftarrows H_2O + CO_2$$
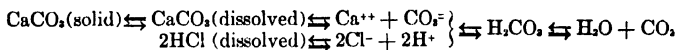
The apparatus shown in Fig. 30 is used.

4. Carbon dioxide is formed in decay (p. 41) and, as Black likewise discovered, in fermentation (see p. 532). Large quantities are collected for industrial use from the vats in which near-beer is brewed.

Physical Properties. — Carbon dioxide is a colorless, odorless gas. It is heavier than air. Its critical temperature is 31.35° (p. 55). The solid melts at − 56°, having a vapor pressure of 5.3 atmospheres. The sp. gr. of the liquid at 0° is 0.95. At 0° its

vapor tension is 35.4 atmospheres and at 20°, 59 atmospheres. It must be preserved, therefore, in very strong cylinders of mild steel. Large quantities of it are sold in such cylinders, and used in making aerated waters. When the liquid is allowed to flow out into an open vessel or, still better, into a cloth bag (non-conductor of heat), it cools itself by its own evaporation and forms a white, snowlike mass. Solid carbon dioxide evaporates under atmospheric pressure at − 79°, without melting.

The solid is used in the laboratory as a cooling agent, being often mixed with ether or alcohol to give closer contact with the vessel containing the substance to be cooled. Mercury (m.-p. − 40°) is easily frozen by the mixture.

Carbon dioxide gas dissolves in its own volume of water (760 mm. and 15°). Up to four or five atmospheres Henry's law (p. 157) 'describes its solubility accurately. An aqueous solution, under a pressure of 3–4 atmospheres, is familiarly known as **soda water**, or carbonated water.

Chemical Properties. — Carbon dioxide is a stable compound. At 2000° and 760 mm., the dissociation reaches 1.8 per cent, or about the same as that of water: $2CO_2 \rightleftarrows 2CO + O_2$.

The more active metals, like magnesium, burn brilliantly when ignited in a hollow lump of solid carbon dioxide, producing the oxide and free carbon. Less active metals, such as zinc and iron, when heated in a stream of the gas, give an oxide of the metal and carbon monoxide.

Carbon dioxide unites directly with many oxides, particularly those of the more active metals, such as the oxides of potassium, sodium, calcium, etc. Hence the decomposition of calcium carbonate by heating (p. 422) is a reversible action.

Carbon dioxide, when dissolved in water, forms an unstable acid:

$$H_2O + CO_2 \rightleftarrows H_2CO_3, \text{ or } \begin{array}{c} H \\ H \end{array}\!\!\Big\rangle O + C\Big\langle\!\!\begin{array}{c} O \\ O \end{array} \rightarrow \begin{array}{c} H-O \\ H-O \end{array}\!\!\Big\rangle C = O.$$
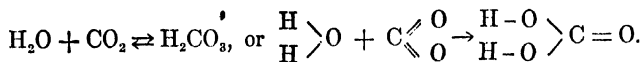
The name carbonic acid is frequently, though improperly, given to the anhydride CO_2, which has no acid properties.

Chemical Properties of Carbonic Acid H_2CO_3. — The solution of carbon dioxide in water exhibits the properties of a very weak acid. It conducts electricity, although not well. It turns litmus red. The ionization takes place chiefly according to the equation:

$$H_2CO_3 \rightleftarrows H^+ + HCO_3^-.$$
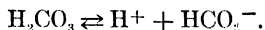
The further ionization of HCO_3^- into H^+ and $CO_3^=$ is exceedingly minute.

Carbonates and Bicarbonates. — When excess of an aqueous solution of carbonic acid is mixed with a solution of a base like sodium hydroxide, or, as the operation is more usually performed, when carbon dioxide is passed into a solution of the alkali, until the liquid is saturated, water is formed and the acid carbonate (**bicarbonate**) of sodium remains dissolved:

$$H_2CO_3 + NaOH \rightleftarrows H_2O + NaHCO_3.$$
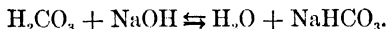
Although the bicarbonate is technically an acid salt, its solution is very weakly alkaline (compare sodium acid sulphide, p. 325). By addition of an equivalent of sodium hydroxide, the normal carbonate is obtained:

$$NaOH + NaHCO_3 \rightleftarrows H_2O + Na_2CO_3.$$
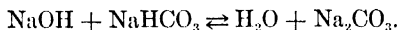
This solution, like that of all normal salts of a strong base and a feeble acid (see p. 324), is decidedly alkaline in reaction.

The **normal carbonates**, with the exception of those of potassium, sodium, and ammonium, are insoluble in water, and may be obtained by precipitation when the proper ions are employed. For example:

$$BaCl_2 + Na_2CO_3 \rightleftarrows BaCO_3 \downarrow + 2NaCl.$$
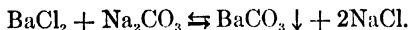
The aqueous solution of carbon dioxide interacts with solutions of barium and calcium hydroxides in a similar manner:

$$Ca(OH)_2 + H_2CO_3 \rightleftarrows CaCO_3 \downarrow + 2H_2O.$$
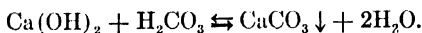
These precipitations are used as **tests** for carbon dioxide or carbonates.

Excess of carbon dioxide converts calcium carbonate into the more soluble bicarbonate, and hence considerable quantities of "lime" are frequently held in solution by natural waters (see hardness, p. 501) which contain carbon dioxide in solution:

$$H_2CO_3 + CaCO_3 \rightleftarrows Ca(HCO_3)_2.$$
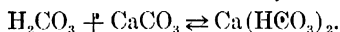
In the same fashion, the carbonates of iron ($FeCO_3$), magnesium, and zinc are somewhat soluble in water containing free carbonic acid. In fact, the solution, transportation, and deposition of all these carbonates take place in nature on a large scale by the alternate progress and reversal of this action.

Uses of Carbon Dioxide. — The use of the gas for impregnating aerated waters has been mentioned. The gas is used in immense quantities in the manufacture of sodium bicarbonate $NaHCO_3$ (baking soda), of sodium carbonate $Na_2CO_3,10H_2O$ (washing soda), and of white lead, a basic carbonate of lead $Pb_3(OH)_2(CO_3)_2$.

Since carbon dioxide is already fully oxidized, it does not burn, and since it is very stable, ordinary combustibles will not burn in it. A small percentage of it will destroy the power of air to support combustion. For this reason, portable **fire extinguishers** contain a dilute solution of sodium bicarbonate and a bottle of sulphuric acid. When the tank is inverted, the acid flows into the solution:

$$2NaHCO_3 + H_2SO_4 \rightleftarrows Na_2SO_4 + 2H_2CO_3 \rightleftarrows 2H_2O + 2CO_2.$$
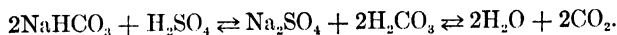
The liquid is saturated with the gas and the excess, rising to the top, by its pressure forces the solution out through the nozzle. The liquid is more effective than an equal amount of water, because the carbon dioxide it carries mixes with the surrounding air.

The most wonderful chemical change which carbon dioxide undergoes is the action by which *plants use it as food.* This important action is discussed in detail in a later chapter (**p. 512**).

CARBON MONOXIDE CO

Preparation. — Carbon monoxide CO is most easily prepared in the laboratory by heating *formic acid* (or sodium formate, a white crystalline solid) with concentrated sulphuric acid. The latter combines with the water, but is not otherwise changed:

$$HCO_2H \rightarrow CO + H_2O.$$
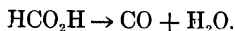
When coke, or any form of carbon burns *with a limited supply of air*, or oxygen, the same gas is produced:

$$2C + O_2 \rightarrow 2CO.$$
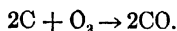
The gas therefore rises from the surface of a coal fire, sometimes escaping unburned, but often burning with a blue flame above the coal.

Producer Gas and Water Gas. — When air is led through burning coke, the mixture of carbon monoxide (40 per cent) with nitrogen (60 per cent) obtained is called **producer gas.** It is combustible, and is used in industrial establishments for heating and to drive gas engines for power.

Commercially, large amounts of carbon monoxide mixed with hydrogen **(water gas)**, are manufactured by *blowing steam over white hot coke* or anthracite:

$$C + H_2O \rightarrow CO + H_2 - 29,100 \text{ calories.}$$
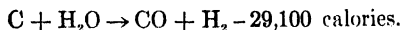
The coke is first set on fire in a brick-lined cylindrical structure and brought to vigorous combustion by blowing in air for ten minutes. Then steam is substituted for the air.

The interaction, as the equation shows, takes place with absorption of heat. Hence, at the end of a few minutes, the coke becomes too cool. It is then necessary to turn the steam off and to turn the air on again, and so on alternately. The mixture of carbon monoxide (40 to 50 per cent) and hydrogen (45 to 50 per cent), containing also some carbon dioxide (4 to 7 per cent), nitrogen (4 to 5 per cent), and oxygen (1 per cent), is known as **water gas.** It is almost wholly combustible, burning with a blue flame, and is used as a source of heat and, by driving internal

combustion engines, to furnish power. It is used also in manu-
facturing illuminating gas (see p. 445).

If both air and steam are driven *together* over the burning
coke, the air enables the coke to burn continuously, and a fuel
gas which is a cross between producer gas and water gas is
obtained.

Fuel gases are employed on a large scale in steel works and
other industrial plants. They give a uniform and easily regu-‑
lated heat, they leave no ash, and their use involves no labor
for stoking.

Industrial Hydrogen from Water Gas. — Hydrogen is re-
quired in large quantities in chemical industry for the manufac-
ture of *ammonia* (p. 380) and for *hydrogenating oils* (p. 547).
It is essential that this hydrogen should be carefully purified
from traces of other gases, such as carbon monoxide and sulphur-
etted hydrogen, which act as poisons on the catalysts employed
in the above processes. The cheapest source of industrial hydro-
gen is *water gas*, and much work has been done to devise a
method for eliminating the undesirable carbon monoxide from
this.

When a mixture of water gas (substantially $H_2 + CO$) and
superheated steam is passed over a suitable catalyst, such as
iron oxide, a reaction occurs as follows:

$$CO + H_2O \rightleftarrows CO_2 + H_2 + 9,800 \text{ calories.}$$
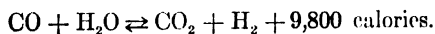
The reaction being reversible, and exothermic in the forward
direction, its equilibrium point is displaced towards the left,
favoring the backward reaction, as the temperature is raised.
It is therefore desirable to work the process at as low a tem-
perature as possible. With iron oxide alone as a catalyst, how-
ever, the interaction between the gases becomes too slow to be
effective at temperatures much below 600°. The addition of
small quantities of other oxides, such as nickel oxide and chro-
mium oxide, has been found to increase the activity of the
catalyst very considerably. Substances which act in this manner
(catalyzing a catalyst, so to speak) are termed **promoters.**

In actual practice the reaction, carried out at 450–500°, gives

a mixture of gases containing only about 2 per cent residual CO. Excess of steam is employed to drive the equilibrium as far as possible towards the right, but the excess of hydrogen present in the original water gas favors, of course, the opposite reaction (compare p. 209). It should be noted that nearly *twice* as much hydrogen as was contained in this water gas is obtained by the process, the second half being derived from the decomposition of the steam.

The bulk of the carbon dioxide present in the final mixture (approximately 30 per cent by volume) is removed by washing the gas with water under pressure. The last traces of carbon dioxide are absorbed by means of lime or alkalies. The removal of the 2 per cent residual CO presents difficulties. Absorption of CO by hot caustic soda solutions and by ammoniacal solutions of cuprous salts has been employed. The most efficient method, however, consists of **preferential combustion** of CO to CO$_2$ with the requisite quantity of air or oxygen in the presence of a second oxide catalyst. If due precautions are taken, CO burns almost quantitatively to CO$_2$ without any H$_2$ present burning to H$_2$O. The small amount of CO$_2$ formed is then removed as already described.

Physical Properties of Carbon Monoxide. — Carbon monoxide is a *colorless, odorless,* and *tasteless* gas. It is *a little lighter* than air (mol. wt. 28), and is very slightly *soluble* in water. It is difficult to *liquefy.* Its boiling-point, when liquid, is – 190°, close to that of liquid air.

Chemical Properties. — All the chemical properties of carbon monoxide are referable to the fact that in it the element carbon appears to be bivalent: C=O. The compound is in fact unsaturated, and combines with oxygen, chlorine, and other substances directly. Thus the gas burns in the air, uniting with oxygen to form carbon dioxide. Iron (p. 693) is manufactured by the reduction of the oxides of iron by gaseous carbon monoxide in the blast furnace.

In sunlight carbon monoxide unites directly with chlorine to form **carbonyl chloride** (phosgene) COCl$_2$. It unites with nickel

and iron to form nickel carbonyl and iron carbonyl (see p. 706), respectively.

Physiological Properties. — The gas is an active poison, and 1 volume in 100,000 volumes of air produces symptoms of poisoning, while 1 volume in 750 to 800 volumes produces death in about thirty minutes. The gas combines. with the hæmoglobin of the blood corpuscles,' forming a stable' compound, and thus preventing the absorption of oxygen by the blood (p. 41). This gas is the chief poisonous substance in illuminating gas. The poisonous effect of tobacco smoke, particularly when inhaled, is due mainly to the carbon monoxide produced by the necessarily incomplete combustion.

Combustions or explosions in confined spaces (such as in a mine-shaft, or in the interior of a warship during an engagement) may cause many deaths through CO poisoning. Gas masks for use in rescue work in such cases are fitted with canisters containing a mixture of metallic oxides, as MnO_2, CuO, Co_2O_3 and Ag_2O (hopcalite). A mixture of this kind acts catalytically, any carbon monoxide passing into the canister being oxidized to carbon dioxide by the oxygen of the air.

Exercises. — 1. (a) What physical property of graphite enables it to cover the surface of a stove so effectively? (b) How does "polishing" with a brush contribute to the result? (c) Why not use paint on a stove? (d) Explain why graphite can be used as a lubricant.

2. If a metal formed the positive electrode (anode) in electrolyzing sodium chloride solution, what chemical change might it undergo (p. 180), and which metals would be least rapidly attacked? What objection is there to using the latter metals in practice?

3. When one cubic meter of oxygen acts upon carbon, what volumes (at the same temperature and pressure): (a) of carbon dioxide; (b) of carbon monoxide can be obtained?

4. Make equations for: (a) the formation of methane by union of carbon and hydrogen; (b) the reduction of stannic oxide (SnO_2) by carbon.

5. Make equations for: (a) the action of sulphuric acid upon calcium carbonate; (b) carbon dioxide on potassium hydroxide solution; (c) the burning of aluminium in carbon dioxide.

6. What are the exact relative weights of equal volumes of carbon dioxide, carbon monoxide, air, and steam?

7. Why does soda water remain quiescent in the closed bottle, and why does it effervesce when the bottle is opened?

8. Rewrite the equations on p. 424 in full ionic form.

9. Formulate, in detail, the equations for the hydrolysis of (a) sodium carbonate, (b) sodium bicarbonate in aqueous solution.

10. Assuming that air contains oxygen and nitrogen in the proportion of 1 : 4 by volume, what are the theoretical proportions of carbon monoxide and nitrogen in producer gas?

11. (a) What volume of water gas is produced from each liter of steam, and (b) what is the proportion of the component gases in the product? (c) What impurities should you expect to find in water gas? (d) How should you attempt to separate the components of water gas?

12. Why is water gas an especially valuable source of heat when high temperatures are required?

13. In what respects does the action of hydrochloric acid on calcium carbonate resemble the action of the same acid, (a) on sodium sulphite, (b) on ferrous sulphide?

.CHAPTER XXX

THE HYDROCARBONS AND THEIR DERIVATIVES. FLAME

THE compounds of carbon and hydrogen are called the **hydro-carbons**. Hundreds of different hydrocarbons, containing different proportions of the two elements, are known. The natural oil *petroleum* is a mixture of many substances of this class.

The hydrocarbons fall into several distinct series, the chief one of which contains methane CH_4 as its simplest member. On account of the fact that certain members of this set are found in paraffin, it is commonly known as the **paraffin series**. For the reason that in this series the carbon has all its four valences employed, the members are also called the **saturated hydro-carbons**.

Paraffin or Saturated Series of Hydrocarbons. — The following is a list of seven of the simplest hydrocarbons of this series, and of two of the higher members:

Methane CH_4	b.-p. $-164°$	Hexane C_6H_{14}	b.-p. $71°$
Ethane C_2H_6	$-89.5°$	Heptane C_7H_{16}	$99°$
Propane C_3H_8	$-37°$	Hexadecane $C_{16}H_{34}$	$287.5°$
Butane C_4H_{10}	$+1°$		m.-p. $18°$
Pentane C_5H_{12}	$35°$	Pentatriacontane $C_{35}H_{72}$	m.-p. $74.7°$

After the first four, the names are based on the Greek numerals corresponding to the number of carbon atoms in the molecule. On comparing the formulæ, we observe that in each the number of units of hydrogen is equal to twice the number of carbon units plus two. The general formula is therefore C_nH_{2n+2}. The series affords a striking illustration of the law of multiple proportions. We note, further, that the first four are gases at the ordinary temperature. The members of the series from pentane to penta-decane $(C_{15}H_{32})$ are liquid under ordinary conditions. From

hexadecane onwards they are solids, with higher and higher melt-ing-points.

In these compounds the carbon is quadrivalent, and each sub-stance is related to the preceding one by containing the addi-tional units CH_2. The formulæ of the first three members may be written graphically to illustrate these two facts:

$$
\begin{array}{ccc}
H & H\ \ H & H\ \ H\ \ H \\
| & |\ \ \ | & |\ \ \ |\ \ \ | \\
H-C-H & H-C-C-H & H-C-C-C-H \\
| & |\ \ \ | & |\ \ \ |\ \ \ | \\
H & H\ \ H & H\ \ H\ \ H
\end{array}
$$
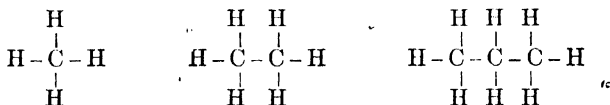
Petroleum. — Petroleum is a thick, greenish-brown oil. When borings are made into the oil-bearing strata, the oil either gushes up, or is pumped to the surface. In the United States many thousands of miles of pipe-lines are used to transport the oil, with the aid of force pumps, to the refineries, and in 1921 nearly 470 million barrels (42 gal. each) were produced. The world's production in 1921 was 760 million barrels.

After the United States, Mexico and Russia are the chief producers of petroleum.

Oil Refining. — The natural oil is a complex mixture, and is partially separated by distillation (p. 82) into products which are still mixtures, but are suited to special purposes. The com-ponents of lower boiling-point come off first and the temperature rises steadily as these components are eliminated and those of higher and higher boiling-point enter the vapor. As certain tem-peratures are reached (or as the sp. gr. of the distillate attains certain values) the condensed liquid is diverted into different vessels, so as to collect together the "fractions" of the same kind. This is called **fractional distillation.**

At some suitable stage, the residual oil is chilled, and a quan-tity of the solid members of the series ($C_{22}H_{46}$ to $C_{28}H_{58}$) crystal-lizes in flakes (*solid paraffin*) and is separated by filtration in presses. The final residue is used for *lubricants* and for *fuel*. The fractions are still mixtures, but contain mainly compounds lying close together in the series. Some of the products are as follows:

Name	Main Components	B.-P.	Uses
Petroleum ether...	Pentane, hexane......	40°– 70°	Solvent,gas-making
Gasoline	Hexane, heptane......	70°– 90°	Solvent, fuel
Naphtha	Heptane, octane......	80°–120°	Solvent, fuel
Benzine	Octane, nonane......	120°–150°	Solvent
Kerosene	,Decane-hexadecane...	150°–300°	Illuminating oil

Vaseline, $C_{22}H_{46}$ to $C_{23}H_{48}$, is separated in some refineries. **Solid paraffin** is employed for waterproofing paper, as an ingredient in candles, and in making chewing gum. **Kerosene,** for oil lamps, is usually the largest fraction. To be employed safely, it should not give any inflammable vapor below 65° (150° F.), which is the legal "flash-point" in many states. Formerly, efforts were made to convert the other less valuable fractions into kerosene. Now the supply largely exceeds the demand, and special methods of treatment (see *cracking*, p. 435) are used to increase the proportion of **gasoline** (petrol), for which there is an ever-increasing need as a motor fuel.

Asphalt, a natural mixture of the solid hydrocarbons, found particularly in Trinidad, is used in road-making.

Oil Shale. — In Scotland, petroleum is also obtained by heating *shale*. The shale is a clay deposit, which contains no oil as such, but which when heated gives off fuel gas, ammonia (see p. 380), petroleum oils, and many valuable hydrocarbon derivatives. The richer shales yield from 30 to 40 gallons of oil per ton. The oil usually contains a much larger percentage of unsaturated hydrocarbons than well petroleum. The yield can be somewhat increased, and the proportion of undesirable unsaturated hydrocarbons diminished, by blowing superheated steam into the retorts during the distillation.

Enormous deposits of oil shale have recently been opened up in the United States, notably in Colorado, Utah, and Nevada. Though at first sight it would appear that the cost of producing oil from shale would prohibit competition with well petroleum, yet the value of the by-products offsets this disadvantage to a large extent. In any case, in view of the apprehended exhaustion of the world's petroleum fields in the near future, these shale deposits constitute a most important national asset.

Natural Gas: Methane CH₄. — Natural gas is obtained from wells, tapping strata close to those which contain petroleum, and in the same localities. It often issues under very high pressure. It owes its combustibility to its chief component (over 90 per cent), **methane** CH_4. It is largely used as a fuel in the regions in which it is found and, in the United States, the annual value of the gas so consumed is nearly \$200,000,000 (1920). The same gas issues from many coal seams ("fire-damp"), and forms explosive mixtures with the air of mines. It rises to the surface when stagnant pools containing decomposing vegetable matter are stirred ("marsh-gas").

The formation of methane by direct union of carbon and hydrogen has already been discussed (p.⁰419).

Methane may be **made** from inorganic materials by the action of water upon aluminium carbide, prepared by the interaction of aluminium oxide and carbon in the electric furnace (see pp. 420-421):

$$Al_4C_3 + 12H_2O \rightarrow 4Al(OH)_3 + 3CH_4.$$
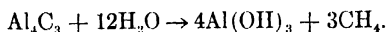
In the *laboratory* the gas is commonly obtained by the distillation of a dry mixture of sodium acetate and sodium hydroxide:

$$NaCO_2CH_3 + NaOH \rightarrow Na_2CO_3 + CH_4.$$
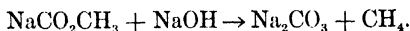
Chemical Properties of the Hydrocarbons. — The hydrocarbons, whether pure or in solution, show *no conductivity* for electricity. They have none of the chemical properties of acids, bases, or salts, and therefore do not enter into double decompositions with substances of these classes. The saturated hydrocarbons are in fact *quite indifferent* to the presence of most chemical reagents.

All the hydrocarbons *burn* with oxygen or air to form carbon dioxide and water:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$
$$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O.$$
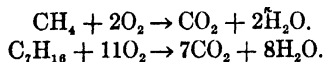
The water can be shown by its condensation on a cold vessel held over the flame. The carbon dioxide gives a precipitate of

calcium carbonate (p. 424) when the gases rising from the flame are drawn through lime-water.

All the hydrocarbons, when *heated strongly* (air excluded), *decompose* or **crack**. They usually lose a part of their hydrogen and become unsaturated. Those of high molecular weight break up to give a mixture of hydrocarbons of low molecular weight. Ethylene C_2H_4, for example, is produced in large amounts by heating the higher members of the series to a red heat. On the other hand, the lower members of the series, when heated, often give compounds of higher molecular weight. Thus, methane gives ethylene and acetylene, along with hydrogen:

$$2CH_4 \rightarrow C_2H_4 + 2H_2.$$
$$2CH_4 \rightarrow C_2H_2 + 3H_2.$$
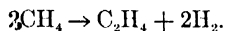
At a white heat all the hydrocarbons decompose into hydrogen and free carbon.

The latter is deposited in a dense form called **gas-carbon,** which is used in making carbon rods for arc lights and electric furnaces, and carbon plates for batteries, and for the electrodes employed in electrolysis. The carbon is ground up, moistened with petroleum residues, subjected to hydraulic pressure and finally heated strongly to expel volatile matter.

Derivatives of the Hydrocarbons. — Although the hydrocarbons are themselves almost inert chemically, yet many important classes of organic substances may be regarded as their derivatives, one or more atoms of hydrogen in the graphic formula (p. 432) being replaced by other elements. The following tabulation should be carefully studied, and the graphic formula of each compound mentioned should be written down by the student.

1. **Halogen Derivatives.** When a mixture of methane and chlorine is exposed to sunlight several successive changes (**substitution** reactions, see p. 183) slowly occur:

$CH_4 + Cl_2 \rightarrow HCl + CH_3Cl$ (methyl chloride)
$CH_3Cl + Cl_2 \rightarrow HCl + CH_2Cl_2$ (methylene chloride)
$CH_2Cl_2 + Cl_2 \rightarrow HCl + CHCl_3$ (chloroform)
$CHCl_3 + Cl_2 \rightarrow HCl + CCl_4$ (carbon tetrachloride).
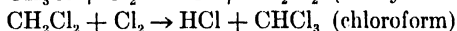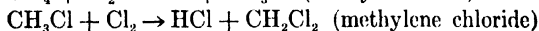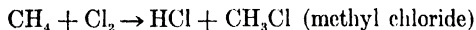
Chloroform $CHCl_3$, used as an anæsthetic, and carbon tetrachloride CCl_4 (p. 420) are familiar substances. Iodoform CHI_3 is employed in surgical dressing. These substances are *not* salts, and are not ionized in solution.

2. Hydroxyl Derivatives (Alcohols). Water acts *slowly* upon methyl chloride, according to the equation:

$$CH_3Cl + H_2O \rightleftarrows HCl + CH_3OH \text{ (methyl alcohol)}.$$
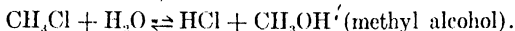
The reaction is reversible and incomplete, but can be accelerated and carried to completion by addition of a base, which removes the HCl as fast as it is formed. Ethyl chloride C_2H_5Cl gives ethyl alcohol C_2H_5OH.

Although containing the radical OH, the alcohols are *not* ionized in solution, and are therefore *not* bases. They are extensively used as solvents for other organic substances (see also p. 533).

3. Oxygen Derivatives (Ethers). When ethyl alcohol and concentrated sulphuric acid are heated to 140°, water and ether $(C_2H_5)_2O$ distil off. The action occurs in two stages:

(1) $C_2H_5OH + H_2SO_4 \rightarrow H_2O + C_2H_5HSO_4$
(2) $C_2H_5HSO_4 + C_2H_5OH \rightarrow H_2SO_4 + (C_2H_5)_2O.$
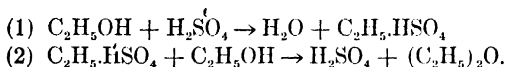
Ether $(C_2H_5)_2O$ is a very volatile and inflammable liquid, used as an anæsthetic and as a solvent for resins, fats and oils.

4. Aldehydes. By fractional combustion of methyl alcohol (passage of a heated mixture of alcohol vapor and air over a metal catalyst), formaldehyde H.CHO is obtained.

$$2CH_3.OH + O_2 \rightarrow 2CH_2O + 2H_2O.$$
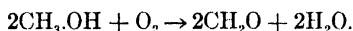
Formaldehyde is a gas. Its solution in water (formalin) is employed as an antiseptic and disinfectant. Its property of hardening gelatins makes it valuable in the leather industry and in the manufacture of artificial silk. It is also used in making dyes and in the production of bakelite (p. 595). The corresponding derivative of ethyl alcohol is acetaldehyde $CH_3.CHO$. The group .CHO is characteristic of aldehydes.

5. Acids. By further partial oxidation, alcohols or aldehydes

give members of the fatty acid series. Thus ethyl alcohol can be *oxidized* directly to acetic acid $CH_3.COOH$ by passing a mixture of the vapor, with air, over specially prepared platinum as a catalyst:

$$C_2H_5.OH + O_2 \rightarrow CH_3.COOH + H_2O.$$
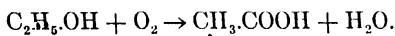
The first acid of this series is formic acid, $H.COOH$ (see p. 426), a corrosive liquid secreted by red ants and present in stinging nettles. Acetic acid (see p. 534) has many industrial uses.

• The lower members of the fatty acid series are perfectly miscible with water, and are slightly ionized in aqueous solution. By neutralization with bases we obtain salts, such as the formates and the acetates. Only the hydrogen of the characteristic .COOH group, it must be noted, is replaceable by metals.

6. **Ketones.** When calcium acetate $Ca(CH_3.COO)_2$ is heated, acetone $(CH_3)_2.CO$ distils off:

$$Ca(CH_3.COO)_2 \rightarrow CaCO_3 + (CH_3)_2.CO.$$
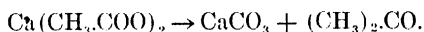
The ketones resemble the aldehydes in many respects, but their characteristic group :CO is not directly combined with hydrogen. Acetone is a liquid boiling at 56°, used in large quantities in the industries as a solvent.

7. **Esters.** Alcohols and acids interact slowly and incompletely to form esters. Thus when ethyl alcohol and acetic acid are used, we obtain ethyl acetate $C_2H_5.COO.CH_3$:

$$C_2H_5.OH + CH_3.COOH \leftrightarrows H_2O + C_2H_5.COO.CH_3.$$
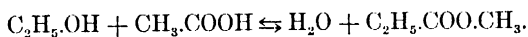
The action may be catalyzed by the addition of a little sulphuric acid.

The equation, as given above, bears certain resemblances to a *neutralization*. It differs sharply, however, from a true neutralization in several respects. An alcohol is *not* a base, neither is an ester a salt. Both classes of substances are non-ionized in solution. True neutralization takes place instantaneously, while the foregoing action, and all like it, proceed very slowly.

The esters form the sweet-smelling constituents of plants. Many are now produced synthetically as substitutes for natural flower and fruit essences.

Unsaturated Hydrocarbons. — In addition to the saturated series of hydrocarbons, several other series are known in which smaller proportions of hydrogen are present. Thus, ethylene C_2H_4, to which illuminating gas largely owes the luminosity of its flame, belongs to a series C_nH_{2n}, all the members of which contain two atoms of hydrogen less than the corresponding compounds of the first series. Again, acetylene C_2H_2 is the first member of a series C_nH_{2n-2}, and benzene C_6H_6 begins a series C_nH_{2n-6}. These are all *unsaturated* because the full valence of the carbon is not in use, and these compounds, therefore, unite more or less readily with hydrogen, chlorine, bromine, and concentrated sulphuric acid. The hydrocarbons of all the series are mutually soluble, but none of them dissolves in water.

Members of the ethylene and acetylene series are found in petroleum, and are formed also to some extent by decomposition during the distillation. As oil containing them acquires dark-colored products by chemical change, the oils are always refined before being sold. They are agitated with concentrated sulphuric acid, which unites with the unsaturated substances and, being insoluble in the oil, collects in a layer below it. The oil is finally washed free from the acid with dilute alkali and with water.

Ethylene C_2H_4. — The formation of one molecule of ethylene from two molecules of methane with elimination of two molecules of hydrogen suggests its graphic formula:

$$
\begin{array}{ccccc}
\text{H} & \text{H} & \text{H}\ \ \text{H} & & \text{H}\ \ \text{H} \\
| & | & |\ \ \ | & & |\ \ \ | \\
\text{H} - \text{C} - \text{H} + \text{H} - \text{C} - \text{H} \rightarrow \text{H} - \text{C} - \text{C} - \text{H} & \text{or} & \text{H} - \text{C} = \text{C} - \text{H} \\
| & | & |\ \ \ | & & \\
\text{H} & \text{H} & &
\end{array}
$$
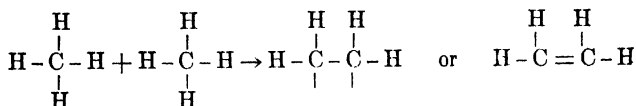
Ethylene is a gas which burns in the air with a highly luminous flame (see p. 443). It combines directly with bromine to form ethylene bromide $C_2H_4Br_2$.

The hydrocarbons of the ethylene series are known as *olefines.* They are of value as illuminants. Their derivatives are similar in character to those of the paraffin hydrocarbons, but are more active chemically in view of their unsaturation. When heated with hydrogen in the presence of a catalyst, such as finely divided

nickel, they give the corresponding saturated derivatives (compare p. 547).

Acetylene C_2H_2. — A mixture, containing acetylene, is formed when any hydrocarbon is heated strongly (p. 419), air being excluded. As in the case of ethylene, the formation from methane by loss of hydrogen (p. 435) suggests the graphic formula:

$$\underset{\overset{|}{H}}{\overset{H}{\underset{|}{H-C-H}}} + \underset{\overset{|}{H}}{\overset{H}{\underset{|}{H-C-H}}} \rightarrow H - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - H \quad \text{or} \quad H - C \equiv C - H$$
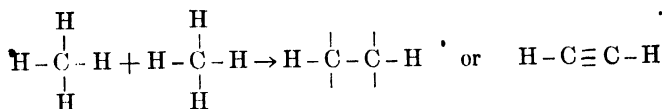
Pure acetylene is prepared by the action of water on calcium carbide (p. 421):

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \uparrow.$$
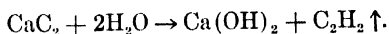
Calcium hydroxide (slaked lime) remains. The gas *burns* with a flame even more luminous than that of ethylene. It is therefore made in generators by the foregoing action for use on automobiles and for lighting buildings remote from a public supply of illuminating gas. Acetylene tanks, which are also in use, contain acetylene dissolved, under high pressure, in acetone.

The Acetylene Blowpipe or Torch. — Acetylene decomposes, when heated, with *liberation* of heat:

$$C_2H_2 \rightarrow 2C + H_2 + 58,100 \text{ cal.}$$
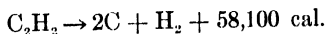
When acetylene burns with oxygen, therefore,

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O,$$
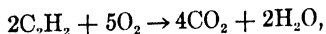
we obtain not only the heat due to the combustion (p. 202) of the carbon to carbon dioxide ($4 \times 96,900$ cal.) and of the hydrogen to water ($116,200$ cal.) but also the heat due to the decomposition of the gas ($2 \times 58,100$ cal.). The temperature of the flame is, therefore, the highest that can be reached by the combustion of any easily obtainable gaseous mixture. The oxyacetylene flame, produced by means of a suitable burner (Fig.

36, p. 67), the gases being furnished from small, portable tanks, is now used for cutting metals. Such a flame will melt its way through a 6-inch shaft of steel, or ·a heavy steel plate several feet wide, in less than one minute, cutting the object in two. Steel buildings have been taken apart rapidly by this device.

Blau gas and **oil gas,** mixtures of hydrocarbons made by "cracking" (see p. 435) heavy oils, are now largely displacing acetylene for uses like those just mentioned. They give flames which are almost as effective, and are more easily controlled. Even the oxy-hydrogen torch is remarkably efficient, when applied to the same purposes.

Benzene C₆H₆. — This is the first member of the *aromatic* hydrocarbon series. It may be synthesized by heating acetylene in a closed vessel at a moderately low temperature: ·

$$3C_2H_2 \rightarrow C_6H_6.$$
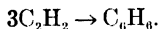
In practice it is obtained, with many of its valuable derivatives, as a by-product in the production of *coke* (p. 538).

The graphic formula of benzene is represented as a closed ring structure:

$$\begin{array}{c}
H \\
| \\
C \\
\diagup\ \diagdown\!\diagdown \\
H - C \quad\quad C - H \\
\parallel \quad\quad | \\
H - C \quad\quad C - H \\
\diagdown\ \diagup\!\diagup \\
C \\
| \\
H
\end{array}$$
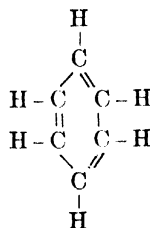
The hydrocarbons of the benzene series exhibit, in fact, many of the properties of *olefines,* combining directly with hydrogen and with the halogens to form saturated compounds such as hexa-hydrobenzene C_6H_{12} and benzene hexabromide $C_6H_6Br_6$.

The second member of the aromatic series is **toluene** $C_6H_5.CH_3$. The third is **xylene** $C_6H_4.(CH_3)_2$. **Naphthalene** $C_{10}H_8$ and **anthracene** $C_{14}H_{10}$ are members of more complex series, containing more than one ring.

Of all hydrocarbons, those of the aromatic series, with their derivatives, are the most important. They are of particular significance in the *dye-stuff* and *explosive* industries, and in the manufacture of synthetic *perfumes* and *drugs*. They give aldehydes, acids, esters, etc., similar to those listed under the paraffin hydrocarbons (pp. 435-437). In addition to these, the following extremely valuable classes of derivatives should be noted:

(1). **Phenols.** The substitution of hydroxyl for a hydrogen atom in benzene gives phenol C_6H_5OH, a substance quite different in many of its properties from an alcohol, although it resembles the alcohols in forming esters with acids (see p. 437). Phenol, when pure, is a colorless solid melting around 40°, with a characteristic odor. It is strongly antiseptic, corrosive and poisonous. In solution it is a *weak acid*.

(2). **Nitro-compounds.** Nitrobenzene $C_6H_5NO_2$ is obtained by the action, of a mixture of concentrated nitric and sulphuric acids upon benzene in the cold:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5.NO_2 + H_2O.$$
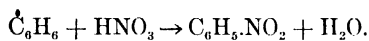
It is a pale yellow liquid, with a smell resembling bitter almonds, and is used in scenting cheap soap.

(3). **Amino-compounds.** Reduction of nitrobenzene by a metal in acid solution gives aniline $C_6H_5.NH_2$. The amino-compounds are derivatives of ammonia, and their solutions accordingly are weakly basic. Aniline, when pure, is a colorless, oily liquid, boiling at 185°. It is the parent substance of the countless aniline dyes.

In subsequent chapters we shall return to the different classes of organic substances, tabulated here and on pp. 435-437, and discuss their properties and industrial uses in greater detail.

FLAME

We have encountered a variety of flames, from the simple one of hydrogen burning in air to the more complicated case of the luminous flame of ethylene or acetylene. The subject will now repay a somewhat closer study.

The Simple Flame. — The flame of hydrogen (giving water), or of carbon monoxide (forming carbon dioxide) is very simple in structure (Fig. 104). We find that there is a tapering column of unburnt gas in the interior, surrounded by a layer of hot gas — the flame itself. The flame is therefore a hollow cone. That the flame is hollow is easily shown by holding a wooden match across it. The match is charred at the two points at which it crosses the flame, and remains unheated in the middle. These flames are simple, because only one chemical change occurs in them. The flames are rather large, because sufficient oxygen to burn all the gas does not reach the latter at once, and the gas travels upwards and diffuses outwards a certain distance before being all consumed.

Fig. 104.

If oxygen is substituted for air, by lowering the jet into a jar of that gas, the flame becomes much smaller. In the absence of atmospheric nitrogen, there is now five times as much oxygen within a given range of the center of the jet as before. This chemical union, like any other, proceeds more rapidly with an increase in the concentration of ' the interacting substances (p. 208). It is therefore completed before the gas has time to diffuse very far from the opening of the jet.

In the chemical point of view, it is a matter of indifference whether the gas outside the flame contains oxygen, and the gas inside consists of substances ordinarily known as combustibles, or whether this order is reversed. In an atmosphere of ordinary illuminating gas, the flame must be fed with air. This condition is easily realized (Fig. 105). The lamp· chimney is closed at the top until it has become filled with illuminating gas. This

Fig. 105.

can be ignited as it issues from the bottom of the wide, straight tube. When the hole in the cover of the lamp chimney is then
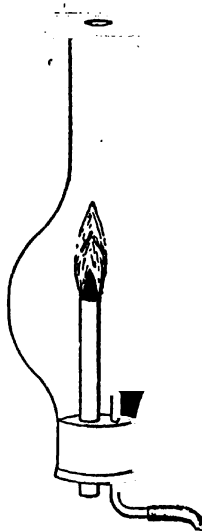
opened, the upward draft causes the flame of the burning gas to recede up the tube, and there results a flame fed by air and burning in coal gas.

Luminous Flames. — The flame of hydrogen, under ordinary circumstances, is almost invisible, nearly all the energy of the combustion being devoted to the production of heat. A part of this, however, may be transformed into light by the suspension of a suitable solid body, such as a platinum wire, in the flame. The holding of a piece of quicklime in an oxyhydrogen flame (see p. 68) is a practical illustration of this method of securing luminosity. In general, luminosity may be produced by the presence of some solid which is heated to incandescence.

In the Welsbach lamp the flame itself is non-luminous and, but for the mantle, would be identical with the ordinary Bunsen flame (see below). The mantle which hangs in the flame, however, by its incandescence, furnishes the light. This mantle is composed of a mixture of 99 per cent thorium dioxide ThO_2 and one per cent cerium dioxide CeO_2. These oxides act as a contact agent, hastening the combustion and liberation of heat close to their surface, and so acquire a temperature higher than the average for the rest of the flame. The Welsbach lamp gives ten times as much light as does an ordinary burner using the same amount of gas.

In cases of brilliant combustion, as of magnesium ribbon or phosphorus, a solid body is formed whose incandescence accounts for the light. The flame of ordinary illuminating gas does not at first sight appear to give evidence of the presence of any solid body. But if a cold evaporating dish is held in the flame for a moment, a thick deposit of finely divided carbon (soot) is formed, and we at once realize that the light is due to the glow of these particles in a mass of intensely hot gas.

The Candle Flame. — A candle is made of a mixture of paraffin and stearic acid (one of the higher members of the fatty acid series, see p. 545). When it burns, the whole phenomenon

is vastly more complicated than the burning of hydrogen. The following are some of the stages in the process, which is operated by the flame's own heat. To start with, the wax is melted and ascends the wick by capillary action. This is merely a physical phenomenon. Then the chemical changes begin. (1) The melted compounds of carbon are decomposed by the heat (*cracked*, p. 435), being turned into more volatile compounds and gases which occupy the central hollow of the flame. (2) The compounds forming the gases and vapors are further decomposed at a white heat, giving free carbon and hydrogen (p. 435). (3) All the materials finally reach a sufficient supply of oxygen and are burned to water and carbon dioxide. There are thus three chemical changes, each of which takes place in a definite region that can be observed by the eye (Fig. 106). The formation of the gases from the melted wax (without gas, there would be no flame) takes place in the dark central region where there is no oxygen. The carbon is set free and glows brilliantly in the luminous cone that surrounds the gas and extends far above it. The final combustion occurs in a fainter cone of flame covering the whole exterior.

Fig. 106.

That there is unburnt gas (produced by decomposition of the wax) in the center is easily shown by inserting a narrow tube, through which some of the gas will ascend. The free carbon in the luminous zone will show its presence by blackening a cold dish placed across the flame.

Lampblack. — When an iron vessel, cooled by a stream of water circulating through it, is suspended in the luminous flame of natural gas or burning petroleum, the carbon (soot) is deposited on the vessel. By rotating the latter, the soot can be continuously scraped off by a stationary piece of metal. The product, **lampblack**, mainly very finely divided carbon, is used in making printers' ink, India ink, and black varnish.

Carburetted Water Gas. — To fit water gas, essentially $H_2 + CO$ (p. 426), which burns with a pale blue flame, for public service as an illuminating gas, unsaturated hydrocarbons, and particularly ethylene C_2H_4, which burn with a highly luminous flame owing to their high carbon content, must be added. The water gas is passed through a tower, filled with strongly heated brick on which oil is continually sprayed. Mixed with the vapor of the oil, the gas goes into the "super-heater," where, at a higher temperature, the decomposition into unsaturated hydrocarbons **(cracking)** takes place. The gas is then cooled and washed to remove the condensible hydrocarbons, which would otherwise collect in the service pipes with resulting waste of combustible material as well as obstruction in the delivery of the gas. A typical carburetted water gas has the composition: Illuminants (largely ethylene) 16.6 per cent; heating gases — methane 19.8 per cent, hydrogen 32.1 per cent, carbon monoxide 26.1 per cent; impurities (nitrogen and carbon dioxide) 5.4 per cent.

Carburetted water gas has now largely supplanted coal gas (p. 537) for lighting and heating purposes.

Non-luminous Gas Flames. — When gas is to be used for heating, the complete combustion of the gas, without any intermediate liberation of free carbon, is desirable. This is achieved in the **Bunsen burner** (Fig. 107) by admitting air at the bottom of the burner, in such a way that the air mixes with the gas before the latter reaches the flame. The air cools the middle zone of the flame, so that at this point the temperature required for dissociating the ethylene, and liberating carbon, is not reached. The oxygen in the air plays no part — mixing carbon dioxide or pure nitrogen with the gas has exactly the same effect. A flame of this kind is non-luminous.

Fig. 107.

Although *the middle zone* of the non-luminous flame *is cooler* than that of the luminous flame, the *average temperature* of the
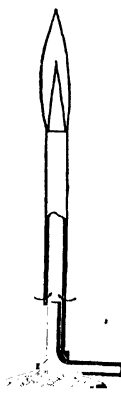
flame as a whole *is higher*. This is the case because the same total amount of heat is liberated in both cases, but the non-luminous flame as a whole is *smaller* in *size*.

The Bunsen type of burner, placed in a horizontal position (Fig. 108) is used in the ordinary **gas cooking range**. As with the Bunsen burner, some .care is required to get good results. The holes which admit the air to the mixer must be kept clear of obstructions, as otherwise luminous flames are produced, smoke and soot are formed, and less heat is generated. The size of the openings must also be adjusted so that the admission of too much air will not cause the flame to flash down the burner and set fire to the gas within.
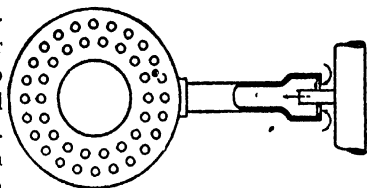
Fig. 108.

The **Meker burner** is an improved type of Bunsen in which this striking back of the flame is prevented by a heavy metal grid clipped over the top of the burner. The principle is the same as that employed in the miner's safety lamp, the metal carrying away the heat so rapidly that the flame is unable to pass through it.

Exercises. — 1. When vegetable matter decays in the air the carbon it contains is finally all turned into carbon dioxide. When the same matter decays under water, it gives methane (p. 434). Explain the difference in the result.

2. What is the density (air $= 1$) of (a) methane, (b) ethylene?

3. Write the graphic formulæ for propane, propyl chloride, propyl alcohol, dipropyl ether, propionaldehyde, propionic acid, dipropyl ketone, propyl propionate.

4. Write the graphic formulæ for toluene, phenol, nitrobenzene, aniline.

5. (a) Given a flame of hydrogen burning in a jar of air, what would be the effect on the flame of lowering the pressure of the air by means of an air pump? (b) What would be the effect on the average temperature of the flame? (c) How about the

heat produced by burning 1 g. of hydrogen in each case? , (*d*) What differences would be observed in using an alcohol lamp at the bottom and on the top of a high mountain?

6. (*a*) In the candle or gas flame, what is the source of the light? (*b*) Why does such a flame become smoky when placed in a draft?

CHAPTER XXXI

SILICON AND BORON

In respect to **chemical relations** there is a close resemblance between silicon and carbon. Silicon gives a monoxide, but is quadrivalent in all its other compounds. It is a non-metallic element.

Occurrence. — Silicon, unlike carbon, is not found in the free condition. In combination it is the most plentiful element after oxygen, and constitutes more than one-quarter of the crust of the earth. The oxide is silica or sand (SiO_2), and this oxide and its compounds are components of many rocks. In the inorganic world silicon is the characteristic element to almost as great an extent as is carbon in the organic realm.

Preparation of Silicon. — When finely powdered magnesium and excess sand are mixed, and one part of the mass is heated, a violent action spreads rapidly through the whole:

$$2Mg + SiO_2 \rightarrow Si + 2MgO.$$
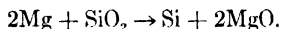
Some magnesium silicide Mg_2Si is formed also. The mixture is treated with a dilute acid which decomposes the magnesium oxide and the silicide, and leaves the **silicon (amorphous)** undissolved. The element is now manufactured at Niagara Falls and elsewhere, by heating sand (SiO_2) with coke in an electric furnace. The process closely resembles that for making carborundum (p. 420), except that less coke is used:

$$2C + SiO_2 \rightarrow 2CO \uparrow + Si.$$
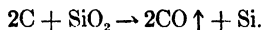
Silicon, as prepared in this way, is a grey, **crystalline** material. **Ferrosilicon** (an alloy of iron and silicon) is made in the same manner by including ferric oxide in the mixture.

Properties. — Amorphous silicon is a brown powder. It unites with fluorine at the ordinary temperature, with chlorine at 430°, with bromine at 500°, with oxygen at 400°, with sulphur at 600°, with nitrogen at about 1000°, and with carbon and boron at temperatures attainable only in the electric furnace. It is dissolved by a mixture of hydrofluoric acid and nitric acid, giving silicon tetrafluoride. **Crystallized silicon** forms needles belonging to the hexagonal system. Silicon and ferrosilicon act readily upon a cold solution of sodium hydroxide (see p. 66), the ortho- or metasilicate of sodium being formed:

$$\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SiO}_3 + 2\text{H}_2 \uparrow.$$
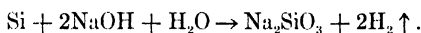
This is one of the sources of hydrogen for filling balloons and airships.

Silicon Tetrachloride and Tetrafluoride. — The tetrachloride SiCl_4 is formed by direct union of the free elements. It is more conveniently prepared by passing chlorine over a strongly heated mixture of silicon dioxide and carbon.

$$2\text{Cl}_2 + \text{SiO}_2 + 2\text{C} \rightarrow \text{SiCl}_4 + 2\text{CO}.$$
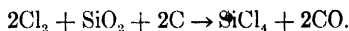
Silicon tetrachloride is a colorless liquid (b.-p. 59°), which fumes strongly in moist air, and with water precipitates silicic acid:

$$\text{SiCl}_4 + 4\text{H}_2\text{O} \rightarrow 4\text{HCl} + \text{Si(OH)}_4 \downarrow.$$
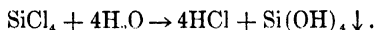
Mixed vapors of SiCl_4, NH_3 and H_2O produce a very dense white *smoke*, consisting of minute particles of NH_4Cl and silicic acid. This smoke was utilized during the war for screening vessels from submarines.

When a concentrated solution of hydrofluoric acid acts upon sand, **silicon tetrafluoride** SiF_4 is liberated:

$$\text{SiO}_2 + 4\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{SiF}_4.$$
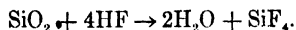
Since the water interacts with the tetrafluoride (see below), the latter is usually made by heating sand with powdered calcium fluoride and excess of concentrated sulphuric acid. In this way

the hydrogen fluoride is generated in contact with the sand, and at the same time the sulphuric acid, operating as a dehydrating agent, renders the water inactive. Hydrofluoric acid acts in a corresponding way upon all silicates, whether these are minerals or are artificial silicates like glass (see p. 283).

Silicon tetrafluoride is a colorless gas. It fumes strongly in moist air, and acts vigorously upon water. This interaction is different from that of the tetrachloride, because the excess of the tetrafluoride forms a complex compound with the hydrofluoric acid:

$$3SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 2H_2SiF_6.$$
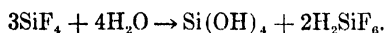
The silicic acid is precipitated in the water, and may be separated by filtration, leaving a solution of **fluosilicic acid.**

This acid is stable only in solution. When the water is removed by evaporation, silicon tetrafluoride is given off, while most of the hydrogen fluoride remains to the last. Its salts are decomposed in a corresponding way when heated. Fluosilicic acid is used in analysis chiefly because its potassium salt K_2SiF_6 is one of the few salts of this metal which are relatively insoluble in water.

Silicon Dioxide SiO₂. — This substance is found in many different forms in nature. In large, transparent, six-sided prisms with pyramidal ends (Fig. 2, p 4) it is known as **quartz** or **rock crystal.** When colored by manganese and iron it is called **amethyst,** when by organic matter, **smoky quartz.** Amorphous forms of the same material, often colored brown or red with ferric oxide, are **agate, jasper,** and **onyx,** the last much used in making cameos. Slightly hydrated varieties of silica are the **opal** and **flint.** Forms produced by organisms are **sponges** and **diatomaceous earth** (Kieselguhr or Tripoli powder). The latter is used in scouring materials and for decolorizing oils (p. 432).

Silica is found in the hard parts of straw and of bamboo. In the form of whetstones it is used for grinding. Pure **sand** (partly disintegrated quartz) is used in glass manufacture (see p. 453) and in many other industries.

Pure quartz can be melted in the oxy-hydrogen blowpipe,

CHEMICAL SMOKE-SCREENS AGAINST SUBMARINES
A VESSEL USING SILICON TETRACHLORIDE

and recently chemical apparatus (**silica ware**) has been made out of it. It has the advantage of being less soluble than glass, and of not breaking even when it is heated white hot and quenched in cold water. Glass breaks when chilled, because the parts first cooled shrink considerably and a great strain is produced. Quartz suffers very little change in volume with change in temperature, and so unequal cooling causes almost no strain. Silica apparatus is more transparent to ultra-violet light than is glass, a property which is utilized in the "quartz mercury lamp."

Silicates. — Silicon dioxide, although differing profoundly from carbon dioxide in its physical nature, nevertheless behaves like the latter chemically. Thus, when boiled with sodium hydroxide solution it forms sodium metasilicate Na_2SiO_3 or orthosilicate Na_4SiO_4.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$
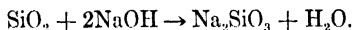
The salt is left as a gelatinous solid ("soluble glass") when the water is evaporated. The silicates of potassium and sodium may also be obtained by boiling sand with the carbonates of these metals, or, more rapidly, usually as metasilicates (see below), by *fusing* the mixture:

$$SiO_2 + K_2CO_3 \rightarrow K_2SiO_3 + CO_2 \uparrow.$$
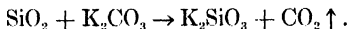
Water glass or soluble glass, being a salt of a feeble acid with an active base, gives a solution with an alkaline reaction (pp. 324-326). As manufactured for commercial use, it contains a considerable excess of silica (mainly in colloidal suspension; see p. 138). It is used as a filler in cheap soaps, for fireproofing and waterproofing timber and textiles, and for preserving eggs.

Silicic Acid H_4SiO_4. — This is an *exceedingly* weak acid. When, therefore, a stronger acid (even carbonic acid will suffice) is added to a solution of sodium silicate, silicic acid is set free. After a little delay it usually appears as a gelatinous precipitate. If, however, the silicate is poured into excess of hydrochloric acid, no precipitation occurs, the silicic acid remaining in **colloidal suspension.** The acid is orthosilicic acid:

$$Na_4SiO_4 + 4HCl \rightarrow 4NaCl + H_4SiO_4 \downarrow,$$
$$Na_2SiO_3 + 2HCl + H_2O \rightarrow 2NaCl + H_4SiO_4 \downarrow,$$
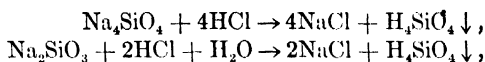
but the gelatinous precipitate, as it dries, gradually loses the elements of water. There seem to be no definite stages, indicating the existence of various acids, such as we observe with phosphoric acid. The final product of drying is the dioxide.

Incompletely dehydrated silicic acid, containing 5–7 per cent of water (**silica gel**), is employed as an adsorbent material for recovering valuable vapors (such as sulphur dioxide, oxides of nitrogen, and volatile organic solvents) from the issuing gases in many large-scale industrial processes. The adsorbed vapors are given up on heating, and the gel is ready for renewed use. Silica gel is also of service in deodorizing petroleum·oils, and as a catalyst (see p. 337).

Mineral Silicates. — While silicic acid is the ortho-acid H_4SiO_4, and no other silicic acids have been made, the salts are most easily classified by imagining them to be derived from various acids representing different degrees of hydration of the dioxide (compare p. 410), or, to put it the other way, different degrees of dehydration of the ortho-acid. The following equations show the relation of the ortho-acid to some of the silicic acids whose salts are most commonly found amongst minerals:

$H_4SiO_4 - H_2O \rightarrow H_2SiO_3$ ($= H_2O,SiO_2$)   Metasilicic acid.
$2H_4SiO_4 - H_2O \rightarrow H_6Si_2O_7$ ($= 3H_2O,2SiO_2$) ⎫
$2H_4SiO_4 - 3H_2O \rightarrow H_2Si_2O_5$ ($= H_2O,2SiO_2$) ⎬ Disilicic acids.
$3H_4SiO_4 - 4H_2O \rightarrow H_4Si_3O_8$ ($= 2H_2O,3SiO_2$)   Trisilicic acid.
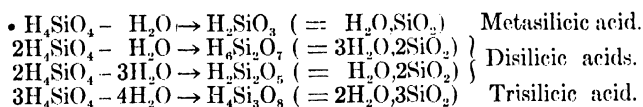
Di- and trisilicates are those derived from acids containing two and three units of silicic anhydride, respectively, in the formula. The valences of the negative radicals of the acids are shown by the number of hydrogen units in the formulæ.

The composition of minerals is often exceedingly complex. This is due to the fact that amongst them mixed salts (p. 247) are very common, in which the hydrogen of the imaginary acid is displaced by two or more metals in such a way that the total quantity of the metals is equivalent to the hydrogen. The fol-

lowing list presents in tabular form some typical or common minerals arranged according to the foregoing classification:

ORTHOSILICATES (H_4SiO_4)   METASILICATES (H_2SiO_3)

Zircon, $ZrSiO_4$ Wollastonite, $CaSiO_3$
Garnet, $Ca_3Al_2(SiO_4)_3$ Beryl, $Gl_3Al_2(SiO_3)_6$
Mica, $KH_2Al_3(SiO_4)_3$ Talc (soapstone), $H_2Mg_3(SiO_3)_4$
Kaolin, $H_2Al_2(SiO_4)_2,H_2O$ Asbestos, $Mg_3Ca(SiO_3)_4$

DISILICATE ($H_6Si_2O_7$)   TRISILICATE ($H_4Si_3O_8$)

Serpentine, $Mg_3Si_2O_7,2H_2O$ Orthoclase (felspar), $KAlSi_3O_8$

Mica, which is obtained in large sheets (see Fig. 1, p. 4) from Farther India, is used in making lamp chimneys and as an insulator in electrical apparatus. **Kaolin,** or **clay,** like mica, is an acid orthosilicate. **Garnets** are pulverized in manganese steel crushers and used in making sandpaper.

Some of these minerals frequently occur mixed together as regular components of certain igneous rocks. Thus, **granite** (p. 4) is a more or less coarse mixture of quartz, mica, and felspar. Frequently the oblong, flesh-colored or white crystals of the last are very conspicuous. **Sandstone** is composed of sand cemented together by clay or by lime, and colored brown or yellow by ferric oxide.

Many minerals consist of solid solutions (see p. 139) of two or more simple silicates. Their compositions cannot therefore be represented by any simple formula.

Glass. — Calcium carbonate (limestone) interacts at a high temperature with sand in the same way as does sodium carbonate:

$$SiO_2 + CaCO_3 \rightarrow CO_2 \uparrow + CaSiO_3$$
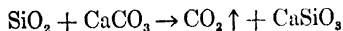
giving **calcium silicate.** Now sodium silicate, when alone, is soluble in water. Calcium silicate is insoluble, but forms a brittle, crystalline mass. By using *both* sodium and calcium carbonates, and employing a larger proportion of sand than that shown in the equation, a material is obtained which has the qualities required in glass. When cooled, the molten mass

becomes viscous and finally, for all practical purposes, solid. Yet it does not crystallize — it is amorphous. It is also practically insoluble in water.

By pouring the viscous material into moulds, or stamping it with dies, articles of *pressed glass* are obtained. Bottles are *blown,* by taking up a sufficient mass of the hot, thick liquid on the end of an iron tube, inserting it in a mould, and blowing until the outline of the mould is filled. *Window glass* is made by blowing an immense, elongated bubble (6 by 1½ ft.), ripping it while still hot and soft, and flattening it out. *Plate glass* for windows and mirrors is manufactured by pouring out the material upon a cast-iron table, with a raised rim, and passing a large, heated iron roller over it. The plate is subsequently ground flat on both sides and polished with rouge (Fe_2O_3).

Soda-calcium glass is called **soft glass,** because it is easily softened by heating. When potassium carbonate is substituted for sodium carbonate, a less fusible substance, used in making some chemical apparatus, and called **hard glass,** is obtained. When lead oxide is employed in place of the limestone, a potassium-lead silicate is formed which, on being cooled, gives **flint glass.** This glass has a higher density and greater brilliancy than soft glass, and is used in making vessels of cut glass and lamp chimneys. The cutting is done with a revolving grinding wheel.

• When glass is allowed to cool quickly, the product is very brittle and apt to crumble to pieces on receiving a shock or scratch. Glassware is therefore all **annealed,** by being passed on a slowly moving frame through a long furnace, which is very hot at the entrance and much cooler at the exit.

Colored glass is made by adding oxides of metals which, with the silica, give colored silicates. Oxide of chromium gives green silicates, oxides of copper and of cobalt blue silicates, and oxide of manganese violet. Gold oxide is reduced to the metal, which remains in colloidal suspension and gives ruby glass. Milky glass is made by adding calcium fluoride, or stannic oxide. The green color of bottle glass is due to iron (ferrous silicate) derived from impure sand or limestone.

The rough surface of **ground glass** is produced with a sand

blast. For **Engraved glass,** the surface is covered by a stencil to protect it from the sand blast, and only the pattern is left exposed.

In **granite iron ware** the surface is covered with a thin layer of easily fusible glass (enamel, see borax).

Pyrex glass, a borosilicate, has also come into extensive use lately for laboratory ware and for cooking vessels. Its low coefficient of expansion renders it much less liable to crack under sudden temperature changes. Like pure silica, it is very resistant to chemicals. It possesses the further advantage of withstanding much greater mechanical shocks.

BORON B

As regards **chemical relations,** boron, being a uniformly trivalent element, is a member of the aluminium family (see Table of periodic system, p. 358). Yet it is a pronounced non-metal, and its oxide and hydroxide are acidic; aluminium is a metal, and with its oxide and hydroxide basic properties predominate. Boron and its compounds really resemble carbon and silicon and their compounds in all chemical properties, excepting that of valence.

Occurrence. — Like silicon, boron is found in oxygen compounds, namely, in boric acid and its salts. Of the latter, sodium tetraborate $Na_2B_4O_7$, or borax, came first from India under the name of **tincal.** It constitutes a large deposit in Borax Lake in California. Colemanite, $Ca_2B_6O_{11},5H_2O$, from California, furnishes a large part of the commercial supply of compounds of boron. The element itself has no applications, and among its compounds only boric acid and its derivatives are of sufficient importance to be discussed here.

Boric Acid and Boron Trioxide. — Boric acid (boracic acid) H_3BO_3 is somewhat volatile with steam, and is found in Tuscany in jets of water vapor (*soffioni*) which issue from the ground. Water, retained in basins of brickwork, is placed over the openings, and from this water, after evaporation, boric acid is obtained in crystalline form. As boric acid is a very feeble acid,

and withal little soluble, it may also be made from sulphuric acid and concentrated borax solution. It crystallizes on cooling the mixture:

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \leftrightarrows Na_2SO_4 + 4H_3BO_3 \downarrow .$$
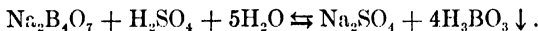
Boric acid crystallizes from water in thin white plates, which are unctuous (like graphite and talc) to the touch. Its solubility in water is 4 parts in 100 at 18°, and 34 in 100 at 100°. The solution scarcely affects litmus. The green tint it confers on the Bunsen flame is used as a test for the acid. At 100° the acid slowly loses water, leaving **metaboric acid** HBO_2, and at 140° **tetraboric acid** is formed: $4HBO_2 - H_2O \rightarrow H_2B_4O_7$. Strong heating gives the **trioxide** B_2O_3, a glassy, white solid. When dissolved in water, all these dehydrated compounds revert to orthoboric acid H_3BO_3. The solution of boric acid in water is used as an antiseptic in medicine (half-saturated, 2 per cent solution), and sometimes as a preservative for milk and other foods.

Borates. — Borates derived from orthoboric acid are practically unknown. The most familiar salt is **borax** or **sodium tetraborate**, which is usually marketed as the decahydrate $Na_2B_4O_7,10H_2O$. In Germany, borax is prepared from boracite $MgCl_2,2Mg_3B_8O_{15}$, found at Stassfurt, by decomposing a solution of the mineral with hydrochloric acid. The boric acid precipitated is dissolved in boiling water, and sodium carbonate is added: $4H_3BO_3 + Na_2CO_3 \rightarrow Na_2B_4O_7 + 6H_2O + CO_2$. In California it is made from colemanite by interaction with sodium carbonate.

Since boric acid is a feeble acid, borax is hydrolyzed by water, and the solution has a marked alkaline reaction (see p. 326).

When heated with oxides of metals, sodium tetraborate behaves like sodium metaphosphate (see p. 413), and is used in the form of **beads** in analysis. If its formula be written $2NaBO_2,B_2O_3$ it will be seen that a considerable excess of the acid anhydride is contained in it, and that, therefore, a mixed metaborate may be formed by union with some basic oxide. Thus, with a trace of cupric oxide, the bead is tinged with blue, from the presence of a compound like $2NaBO_2,Cu(BO_2)_2$. In welding iron, borax is scattered on the parts, and combines with the

oxide to form a fusible mixed borate, which is forced out by the pressure. Borax is also mixed with glass in making enamels for cooking utensils.

Exercises. — 1. Compare and contrast the elements carbon and silicon, and their corresponding compounds.

2. What product is obtained by the action of hydrochloric acid on magnesium silicide Mg_2Si (compare p. 434)?

3. Derive the valences of zirconium and of glucinum from the formulæ on p. 453.

4. Compare and contrast the elements boron and silicon, and their corresponding oxygen acids.

5. The inside surface of a bottle containing concentrated sodium hydroxide solution becomes etched and dull. To what is this due?

6. Write an equation for the action of heat upon borax.

CHAPTER XXXII

In the chapters preceding we have classified our substances under one of the particular elements they contained. Thus, chloroform, alcohol, and ether were put under carbon. Hydrogen sulphide and sulphuric acid were considered as compounds of sulphur. Now this classification is of a *theoretical* nature. That chloroform, alcohol, and ether all contain carbon cannot be told by mere *inspection*. We have to make experiments, and to reason about the results, before we reach this inference. Thus we put our *inference* as the title of the chapter, and distributed the observations and data through it. There is, however, another way of classifying the facts, which is just the opposite of this one. It is the *practical* classification. When we obtain a specimen, or when a substance appears in the course of an experiment, we must be able to tell what particular substance it is. If it is a white powder, it may contain almost any of the whole list of elements. It may be any one of several thousands of substances. We can recognize it only by its physical properties (p. 6) and by the physical properties of other substances that we can get from it by interaction with known chemical compounds. We need, therefore, a plan of operation, and this plan must be based upon a *classification by physical properties*, not by constituents.

One benefit of the discussion of such a plan is that it will afford us a *review* of some of the facts already mentioned, by presenting the same facts from a different view-point, and by showing the uses to which they may be put. To avoid unnecessary repetition, we shall refer frequently to the previous statements of the facts. To understand what is here said, therefore, the reader should look up every reference and re-read the statement.

Is the Material a Mixture? — The first question that occurs to us is, whether the material is a single substance or a mixture. When it is a mixture, we can often, though not always, very quickly find this out.

If it is **a solid mass or powder**, we examine it with the naked *eye* and with the help of a *lens*. If we see two or more kinds of particles, as in granite (p. 4), in a mixture of sand and sugar, or in a piece of rusty iron, then it probably is a mixture.

Whether it appears to the eye to be a mixture, or not, we can next try a *solvent*, such as water, ether, or carbon tetrachloride. If a part of a small sample refuses to dissolve (*e.g.* sand), while the rest dissolves (*e.g.* sugar), we have shown that there are two different sets of physical properties, and therefore two different substances (p. 17) present. As there may be very little of the soluble substance in the mixture, we may not perceive at once that anything has dissolved. So we allow a drop of the liquid to evaporate on a clean watch crystal, and observe whether any residue remains.

If the material is **a liquid**, we depend largely on differences in the *volatility* of different substances to find out whether it is a mixture. If a drop evaporates on a watch crystal, leaving a residue (solid or liquid) which does not evaporate, then it is a mixture. If this test fails, because all, or none, evaporates, then we must distil the liquid, with the bulb and most of the stem of a thermometer in the vapor (Fig. 41, p. 82), and note whether the whole comes over at one temperature (single substance, in most cases) or whether the temperature changes as the distillation proceeds (mixture, such as petroleum, p. 432).

These are simply a few examples intended to show how, when a practical problem is before us for solution, we use *physical properties* as the basis of our reasoning and classification.

The Recognition of a Single Substance. — The majority of the substances we have met with are acids, bases, or salts. In identifying a substance of one of these classes, it is convenient to attempt the recognition of the positive and of the negative radicals (or ions) as *two almost separate problems.* In other words,

we investigate one radical at a time. On the other hand, substances which do not belong to any of these classes, such as simple substances (sulphur, carbon, chlorine, etc.), oxides (sulphur dioxide, carbon monoxide, etc.), and many organic substances (*e.g.* carbon disulphide, ethyl alcohol), are investigated as a single problem.

Scope of this Chapter. — In discussing the recognition of a single substance we shall, for the present, limit ourselves to the non-metallic elements. We shall consider the elementary substances themselves (sulphur, oxygen, etc.), the oxides of such elements, the few organic compounds described, the more common non-metallic negative ions, and ammonium-ion. We shall leave out of consideration until later (Chapter L) 'the metallic elements. We shall also ignore the metallic positive radicals, although one of these (or hydrogen-ion) must inevitably be combined with the negative radical under consideration.

External Examination (Solids). — The specimen may be a solid, a liquid, or a gas. We should note in which of these states it exists under room conditions. What follows applies only to *solids* — the liquids and gases will be taken up later.

Without training in crystallography we can tell little about the **crystalline form** (p. 105) of the specimen. But anything conspicuous, such as **needle**-shape or **cubical** formation of the particles, must be noted.

The **color**, if any, is significant. If **yellow**, the specimen may be *sulphur* (p. 317), if **black**, *carbon* (p. 416) if **black** and crystalline, with **violet** vapor, *iodine* (p. 276). Most substances are colorless.

The **odor**, if any, must be noted. Many salts of ammonium (carbonate, sulphide, etc.) smell of *ammonia* (p. 386). Some sulphides (of sodium, potassium, ammonium, etc.) smell of *hydrogen sulphide* (p. 324). Some acetates smell of *acetic acid* and hypochlorites of *hypochlorous acid* (p. 298).* Some chlo-

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* Many experimental details, essential for the successful performance by a beginner of the tests described in this chapter are here omitted. They will be found in the Author's *Laboratory Outline of College Chemistry*.

rides (*e.g.* PCl_5 and $AlCl_3$), in moist air, give *hydrogen chloride*, with the odor and fumes characteristic of that substance.

Effect of Heating (Solids). — A great deal may be learned by heating as much of the specimen as will fill the rounded bottom of a small, dry test-tube.

The substance may *fuse*. Many substances, such as some chlorides and most hydrates, do so. Continue heating.

A **sublimate** (solid deposit on the cold part of the tube) may appear. **Black** crystals (from violet vapor) are *iodine:* **white** crystals, with the limitations we have set, show the substance to be a *salt of ammonium* (p. 386). Confirm by smelling, and by adding sodium hydroxide to the original substance (p. 386). (Salts of mercury sublime also.)

A **reddish-brown liquid** condenses, becoming, when cold, a yellow solid. This is probably *sulphur* from a *sulphide* (such as FeS_2, p. 704).

Water condenses from *hydrates, acid-salts,* and some *organic* compounds. Test the water with litmus paper. An **acid** reaction indicates an *acid-salt* (p. 247), an easily hydrolyzed salt (*e.g.* $FeCl_3,6H_2O$) or an *organic acid.* Continue heating, inclining the tube mouth downwards, removing condensed water with filter paper until no more comes off, and heat the residue.

A **gas** is given off. The gas may be **violet** (some *iodides*) or **brown** (some *nitrates*, p. 392, and some *bromides*). If brown, lower a glass rod dipped in silver nitrate solution into the gas in the tube. Bromine will give a white precipitate (AgBr, p. 275). In case of a negative result try the test for nitrates.

The gas may be **colorless.** If it has an **odor,** it may be ammonia from a *salt* of *ammonium,* sulphur dioxide from a *bisulphite* (p. 333) or from oxidation of a *sulphide* (p. 332). A stifling odor with **fumes** may be sulphur trioxide from some *sulphates* or decomposition products from some *organic* matters.

The gas is **colorless** and **odorless.** It may be oxygen (test with long, glowing splinter of wood) from a *peroxide, chlorate,* or *nitrate* (of K or Na). To learn which of these it is, dissolve or suspend a little of the substance in water, add dilute sulphuric

acid, and test for hydrogen peroxide (p. 292). In case of a negative result examine the residue (as in p. 463).

A **colorless, odorless** gas may be carbon dioxide, coming from a *bicarbonate* or a *carbonate* (except of K or Na). Lower a glass rod dipped in lime-water into the gas in the test-tube (white precipitate, $CaCO_3 \downarrow$).

The substance **carbonizes or chars** and gives an odor of smoldering wood or burning flesh. The compound is *organic*. Identify by properties (pp. 435-437, 441).

Heating may produce **no effect.** On the other hand, *more than one* of these effects (*e.g.* both water and sulphur dioxide from a bisulphite) may be given by the same specimens.

If heating produces any effect, continue heating until all change ceases, and preserve the residue for use in p. 463.

In most cases other distinctive properties and tests will be found on the pages referred to.

Effect of Sulphuric Acid on Solids. — Fill the rounded bottom (only) of a test-tube with the substance, add just enough concentrated sulphuric acid to moisten the sample, and warm slightly.

A **gas** (effervescence) which fumes in the breath may be given off. If the gas is **brown** or **yellow**, it may be bromine (bleaches litmus paper) mixed with hydrogen bromide from a bromide (p. 273). It may be nitrogen tetroxide (odor) from a *nitrate* (p. 390). If **violet,** with brown deposit, accompanied by an **odor** of hydrogen sulphide, it is iodine from an *iodide* (p. 278).

If the gas fumes, but is **colorless,** it may be hydrogen chloride from a *chloride* (add manganese dioxide to get chlorine, p. 178). It may be hydrogen fluoride from a *fluoride* (a moistened glass rod acquires white precipitate of silicic acid produced by decomposition of silicon fluoride, p. 283).

The gas **does not fume.** If **yellow** it may be chlorine from *bleaching powder* (p. 296) or nitrous anhydride from a *nitrite* (p. 399). A *chlorate* also gives a yellow gas (chlorine dioxide ClO_2) when heated with concentrated sulphuric acid. In this case oxygen will have been obtained in the test on page 461.

Heat very carefully, since chlorine dioxide is explosive (stop heating when material in tube begins to crackle!).

The gas does not fume and is colorless. An odor of sulphur dioxide indicates a *sulphite* (p. 333). An odor of hydrogen sulphide indicates a *sulphide*. If the gas is odorless, it may be carbon monoxide (burns, leaving carbon dioxide) from a formate (p. 426), or oxygen from some *oxides* or a *peroxide*, or nitrous oxide from ammonium nitrate (p. 400), or carbon dioxide from a carbonate.

* No gas evolved indicates a *silicate* (p. 451), *sulphate* (p. 347), *phosphate* (p. 412), or a basic *oxide*.

Sulphuric Acid on the Residue from p. 462. — If the substance gave off oxygen when heated alone (p. 461, foot), add a drop or two of concentrated sulphuric acid to the residue. If the specimen now gives a yellow gas (nitrous anhydride), the original substance was a *nitrate* (of K or Na), from which the nitrite was formed by heating (p. 398). If it gives a colorless, fuming gas (HCl), the original substance was a chlorate (p. 310).

Examination of a Liquid. — Test the specimen with litmus paper. A marked acid reaction may be due to an *acid*, an acid-salt (p. 247), or a hydrolyzed salt (p. 326).

If it bleaches litmus paper, it may be *chlorine-water* or *bromine-water* (odor).

If it is markedly alkaline in reaction, it may be a solution of a *base* or a hydrolyzed *salt* (p. 326).

Note the odor. Ammonium hydroxide, hydrogen sulphide solution, sulphurous acid, concentrated nitric acid and concentrated halide acids all have odors. Alcohol, acetic acid, carbon disulphide, carbon tetrachloride, and hydrocarbons (*e.g.* gasoline) have odors easily distinguished from those of the foregoing.

Evaporate a few drops to dryness on a watch crystal. A solid residue shows that the original substance was a *solution* in water (or possibly alcohol or some other solvent, if the vapor has an odor indicating this). If there is a solid residue, a quantity of

it m̧ay be obtained by evaporating a larger amount of the liquid, and may then be treated as a solid (pp. 460-462).

If the specimen leaves **no residue,** and is not acid or alkaline but has an **odor,** it may be one of the volatile organic compounds named above. If it is **odorless,** it may be a solution of hydrogen peroxide (p. 291) or simply pure water.   '

Examination of a Gas. —The gas, has a **color.** A **brown** gas may be *bromine* or *nitrogen tetroxide.* The former liberates iodine from potassium iodide solution (p. 280), but not bromine from a bromide (insert rods moistened with solution of an iodide and a bromide). The latter becomes deeper brown on warming (p. 392). A **greenish-yellow** gas is *chlorine.* It bleaches, and displaces bromine from a solution of a bromide (p. ,275). ·

The gas may **become colored** (yellow or brown) on admitting **air.** It is *nitric oxide* (p. 391).

The gas may have a distinctive **odor.** *Sulphur dioxide, hydrogen sulphide, nitrogen tetroxide,* and *ammonia* are of this kind.

The gas may **fume** in the breath. The *chloride, bromide,* and *iodide* of *hydrogen* do so. · Distinguish by dissolving in a little water and adding, manganese dioxide.

The gas may be **combustible.** Burning with a **blue flame** indicates *hydrogen* (vessel bedewed with moisture), or carbon *monoxide* (leaving carbon dioxide, test, p. 424). Burning with a slightly **luminous flame** indicates *methane* (p. 434) and a very luminous flame (often depositing carbon) indicates *ethylene* (p. 438) or *acetylene* (p. 439).

The gas may **relight a glowing splinter of wood.** This is *oxygen,* or *nitrous oxide* (p. 400). The former, with nitric oxide, gives a brown gas (p. 391), the latter does not.

The gas may give a white precipitate ($CaCO_3$) with lime-water. This is *carbon dioxide.*

The gas having **none** of these properties is *nitrogen* (p. 367).

In most cases other distinctive properties will be found on the pages referred to.

Exercises. — 1. Look up the references, and give the properties (physical as well as chemical), other than those mentioned in

p. 460, by which you should recognize: (a) sulphur, (b) carbon, and (c) iodine.

2. Same question in regard to: (a) ammonia, (b) hydrogen sulphide, and (c) hypochlorous acid.

3. Same question in regard to: (a) an acid salt, (b) a hydrate, (c) nitrogen tetroxide, (d) bromine, (e) sulphur trioxide, (f) hydrogen peroxide, (g) ammonium nitrate, (h) carbon dioxide.

4. Same question in regard to (p. 462): (a) a bromide, (b) an iodide, (c) a nitrate, (d) bleaching powder, (e) sulphur dioxide, (f) carbon monoxide, (g) a silicate, (h) a sulphate, and (i) a phosphate.

5. Same question in regard to (p. 463): (a) conc. and (b) dil. sulphuric acid, (c) conc. and (d) dil. nitric acid, (e) conc. and (f) dil. hydrochloric acid, (g) hydrobromic acid, (h) hydriodic acid, (i) phosphoric acid, (j) sulphurous acid.

6. Same question in regard to: (a) chlorine-water, (b) alcohol, (c) acetic acid, (d) carbon disulphide, (e) carbon tetrachloride, (f) a hydrocarbon.

7. Same question in regard to: (a) nitric oxide, (b) hydrogen, (c) methane, (d) ethylene, (e) acetylene, (f) nitrous oxide, (g) ozone, (h) nitrogen.

8. Why does sodium sulphide smell of H_2S (see pp. 154, 324)?

9. When ammonium nitrate is heated in a test-tube, the gases evolved do not relight a glowing splinter. How can this be reconciled with p. 400?

CHAPTER XXXIII

THE METALLIC ELEMENTS

In developing the chemistry of the metallic elements, we shall naturally take as much advantage as possible of the *classification of the metals into families*, as given in the table of the Periodic System on p. 358. The consideration of each family separately will enable us to bring out very clearly the outstanding similarities in chemical behavior of the various elements comprised in it, the gradations in their properties and in the properties of their compounds, and the occasional lapses of the more original members from the family standards.

In some cases we shall find these lapses so serious that it becomes necessary to disregard the periodic arrangement altogether, and to utilize other methods of grouping the elements. The main defects in the periodic system have already been noted (p. 363), and the reader should pay particular attention, at this point, to the possibility of employing the *activity order of the metals*, in which many features in the behavior of metals and their compounds are summed up, as an alternative means of classification.

Before we take up any particular group of the metals in detail, however, a preliminary survey of the characteristic properties of the whole community will be of value.

Physical Properties of the Metals. — Metals show what is commonly called a **metallic luster**, but, as a rule, they do so only when in compact form. Magnesium and aluminium exhibit it when powdered, but in this condition most metals appear black.

The metals can all be obtained in **crystallized form**, when a fused mass is allowed to cool slowly and the unsolidified portion is poured off. In almost all cases the crystals belong to the regular system.

The metals vary in **specific gravity** from lithium, which is little more than half as heavy as water (sp. gr. 0.59), to osmium, whose specific gravity is 22.5. Those which have a sp. gr. less than 5 are called the **light metals**, and the others the **heavy metals**.

Most metals are **malleable**, and can be beaten into thin sheets without loss of continuity. Those which are allied to the non-metals, however, such as arsenic, antimony, and bismuth, are brittle. The order of the more important elements in respect to this property, beginning with the most malleable, is: Au, Ag, Cu, Sn, Pt, Pb, Zn, Fe, Ni.

The **tenacity** of the metals places them in an order different from the above. It is measured by the number of kilograms which a piece of the metal 1 sq. mm. in section can sustain without breaking. Some values are as follows: Fe 62, Cu 42, Pt 34, Ag 29, Au 37, Al 20, Zn 5, Pb 2.

The **hardness** is measured by the ease with which the material may be scratched by a sharp, hard instrument. Potassium is as soft as wax, while chromium is hard enough to cut glass.

The **temperature** at which the metal **fuses** has an important bearing on its manufacture. Most of the following **melting-points** are taken from a table issued by the United States Bureau of Standards:

Metal	Temp	Metal	Temp	Metal	Temp
Mercury	-39°	Zinc	419°	Cast iron	1150°
Potassium	62°	Antimony	630°	Manganese	1260°
Sodium	96°	Magnesium	651°	Nickel	1452°
Tin	232°	Aluminium	659°	Chromium	1520°
Bismuth	271°	Silver	960°	Iron (pure)	1530°
Cadmium	321°	Gold	1063°	Platinum	1755°
Lead	327°	Copper	1083°	Tungsten	3350°

The methods of manufacture and the treatment of metals are much influenced also by their **volatility**. The following are easily distilled: Mercury, b.-p. 357°; potassium and sodium, b.-p. about 700°; cadmium, b.-p. 770°; zinc, b.-p. 920°. Even the most involatile metals can be vaporized in the electric arc.

The good **conductivity** of metals for **electricity** distinguishes them with some degree of sharpness from the non-metals. They show considerable variation amongst themselves, silver conducting sixty times as well as mercury. The following table gives

the conductivities of the metals, expressed in terms of the number of meters of wire 1 sq. mm. in section which, at 18°, offer a resistance of one ohm:

Copper, annealed	62.9	Platinum		9.1
Silver, 99%	60.2	Nickel, 97%		8.5
Copper, drawn	56.2	Iron (0.1% C)		8.3
Gold	41.3	Steel (0.1% C)		5.0
Aluminium, 99%	34.0	Lead		4.8
Zinc, pure	16.4	Mercury		1.05
Brass (70% Cu, 30% Zn)	15.1	Bismuth		0.84

To compare these **conductivities** with those of solutions, it may be said that decinormal hydrochloric acid (p. 243) has a conductivity on the above scale of 0.035, or a thirtieth of that of mercury. Metallic conduction of electricity is due entirely to the **transfer of electrons through the material;** *there is no decomposition as in the case of solutions.*

The metals are also, in general, good **conductors of heat.** Silver, copper and aluminium, in the order named, possess the highest values for this property.

General Chemical Relations of the Metallic Elements. — Since most of the compounds of the metals are electrolytes, their aqueous solutions, except when the metal is a part of a compound ion, all contain the metal largely in the ionic state, and the resulting substances, such as potassium-ion and cupric-ion, have constant properties, irrespective of the nature of the negative ion with which they may be mixed. The properties of the ions, simple and compound, are much used in making tests in analytical chemistry. On the other hand, the chemical properties of the oxides and of the salts in the *crystalline state* are of importance in connection with metallurgy.

There are **three chemical properties** which are **characteristic of the metallic elements.** All of them have already been discussed somewhat fully.

1. The metals are able by themselves to form *positive* radicals of salts, and therefore to exist alone as positive ions (**pp. 222, 355**).

2. The oxides and hydroxides of the metals are **basic** (**pp. 83, 247**).

3. Each *typical* metal forms compounds with the halogens which, in the presence of excess of the corresponding halogen acid, are not extensively (often not even appreciably) hydrolyzed by water. The same thing is true of other compounds of the metals with negative radicals derived from active acids, such as the nitrates or sulphates.

In reference to the third characteristic, the **non-hydrolysis of halides of typical metals,** a word of explanation is required. **Active bases** (hydroxides of typical metals), such as sodium hydroxide, give, with **feeble acids,** salts whose solutions are **alkaline in reaction.** This is due, as we have already explained (p. 324), to partial hydrolysis. In the same way, the **less active bases,** in other words the hydroxides of less active metallic elements, give, with active acids, salts whose solutions are not neutral, but **acid in reaction.** Thus cupric chloride solution is feebly acid, since cupric hydroxide is a very weak base:

$$CuCl_2 \rightleftarrows Cu^{++} + 2Cl^-$$
$$2H_2O \rightleftarrows 2OH^- + 2H^+$$
$$Cu(OH)_2 \qquad 2HCl$$
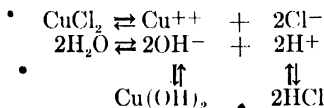
Where hydrolysis is appreciable and the base formed is only very slightly soluble, as in the case of aluminium chloride, the reaction tends to go forward continuously through precipitation of the hydroxide. Accumulation of hydrogen-ion in the solution, however, acts as a counterbalancing factor, diminishing hydroxyl-ion concentration and preventing complete hydrolysis. Any hydroxide precipitated, indeed, may always be brought back into solution by addition of a concentrated solution of the active acid involved.

The halogen compounds of typical non-metals, on the other hand, such as PCl_3 and $SiCl_4$, are *completely decomposed by water* (see pp. 409, 449), and the hydrolysis cannot in such instances be reversed, however great a concentration of the halogen acid is added. The hydroxide produced is here itself acidic, such as H_3PO_3, H_4SiO_4. That the line between metals and non-metals is not perfectly distinct, nevertheless, may be seen by reference to the case of tellurium (p. 354). Other examples of

elements on the borderline between metals and non-metals will be met with later in the arsenic family (Chapter XLVII).

Salts formed by the interaction of *active* bases with *active* acids exhibit, as has already been explained (p. 324) no signs of hydrolysis in aqueous solution. With salts derived from a base and an acid, both of which are weak, however, the extent of hydrolysis is inevitably very considerable. If either the resulting acid or the resulting base is insoluble, hydrolysis will go on to completion. Aluminium carbonate and ammonium silicate are examples.

Occurrence of the Metals in Nature. — The minerals from which metals are extracted are known as **ores.** They present a comparatively small number of different kinds of compounds. Most of the metals are found in more than one of these forms, so that in the following statement the same metal frequently occurs more than once.

When the metal occurs free in nature, it is said to be **native.** Thus we have gold, silver, the platinum family, copper, mercury, bismuth, antimony, and arsenic occurring native (see p. 65).

The metals whose **oxides** are important minerals are iron, manganese, tin, zinc, copper, and aluminium. The metals are obtained commercially from the oxides in each of these cases.

The metals whose **sulphides** are used as ores are iron, nickel, cobalt, antimony, lead, cadmium, zinc, copper, and mercury.

From the **carbonates** we obtain iron, lead, zinc, and copper. Several other metals, such as manganese, magnesium, barium, strontium, and calcium occur in larger or smaller quantities in the same form of combination.

The metals which occur as **sulphates** are those whose sulphates are not freely soluble, namely lead, barium, strontium, and calcium.

Compounds of metals with the **halogens** are not so numerous. Silver chloride furnishes a limited amount of silver. Sodium, potassium and magnesium chlorides are found in the salt-beds.

The natural **silicates** are very numerous, but few are used for the preparation of the metals.

Methods of Extraction from the Ores. — The art of extracting metals from their ores is called **metallurgy.** Where the metal is **native,** the process is simple, since melting away from accompanying "gangue" is all that is required. Frequently a **flux** is added. A flux usually is a substance which interacts with infusible materials to give fusible ones. It combines with the gangue, giving a fusible **slag** (resembling glass). Since the slag is a melted salt, usually a silicate, and does not mix at all with the molten metal, separation of the products is easily effected. When the ore is a *compound,* the metal has to be liberated by our furnishing a material capable of combining with the other constituent. The details of the process depend on various circumstances. Thus the volatile metals, like zinc and mercury, are driven off in the form of vapor, and secured by condensation. The involatile metals, like copper and iron, run to the bottom of the furnace and are tapped off.

Where the ore is an **oxide** it is usually reduced by heating with carbon in some form. This holds for the oxides of iron and copper. Some oxides are not reducible by carbon in an ordinary furnace. Such are the oxides of calcium, strontium, barium, magnesium, aluminium, and the members of the chromium group. At the temperature of the electric furnace even these may be reduced, but the carbides are formed under such circumstances, and the metals are more easily obtained otherwise. Recently, heating the pulverized oxide with finely powdered aluminium has come into use, particularly for operations on a small scale. Iron oxide is easily reduced by this means, and even the metals manganese and chromium may be liberated from their oxides quite readily by this action. On account of the great amounts of heat liberated, this procedure has received the name **aluminothermy** (see p. 583).

When the ore is a **carbonate,** it is first heated strongly to drive out the carbon dioxide (see p. 422): $FeCO_3 \rightleftarrows FeO + CO_2\uparrow$, and then the oxide is treated according to one of the above mentioned methods. When the ore is a **sulphide,** it has to be calcined (p. 332), in order to remove the sulphur, and the resulting oxide is then reduced.

Chlorides and fluorides of the metals can be decomposed by heating with metallic sodium. This method was formerly employed in the making of magnesium and aluminium.

The metals which are not readily secured in any of the above ways can be obtained easily by **electrolysis** of the fused chloride or of some other compound. Aluminium is now manufactured entirely by the electrolysis of a solution of aluminium oxide in molten cryolite.

Compounds of the Metals: Oxides and Hydroxides. — The **oxides** may be made by direct burning of the metal, by heating the nitrates (see p. 392), the carbonates (see p. 422), or the hydroxides (see p. 60). Most oxides are practically insoluble in water, although the oxides of the metals of the alkalies and alkaline earths interact with water rapidly to give the hydroxides. Oxides are usually stable. Those of gold, platinum, mercury, and silver decompose readily when heated, but as we go up the electromotive series of the metals (p. 240), the difficulty of decomposing their oxides by heat rapidly increases (see p. 206). The metals, like the non-metals, frequently give several different oxides. Those of the univalent metals (having the form K_2O), if we leave cuprous oxide and aurous oxide out of account, have the most strongly basic qualities. Those of the bivalent metals of the form MgO are also predominantly base-forming. Those of the trivalent metals of the form Al_2O_3, known as **sesquioxides** (Latin, *sesqui-*, one-half more), are the least basic of the basic oxides. The oxides of the forms SnO_2, Sb_2O_5, CrO_3, and Mn_2O_7, in which the metals have valences from 4 to 7, are mainly acid-forming oxides, although the same elements usually have other lower oxides, which are basic.

The **hydroxides** are formed, in the cases of the metals of the alkalies and alkaline earths, by direct union of water with the oxides. They are produced also by double decomposition when a soluble hydroxide acts upon a salt (see p. 171). All hydroxides, except those of the alkali metals, lose the elements of water when heated, and the oxide remains. In some cases the loss takes place by stages, just as was the case with orthophosphoric acid (p. 410). Thus lead hydroxide $Pb(OH)_2$ first gives the hy-

droxide $Pb_2O(OH)_2$, then $Pb_3O_2(OH)_2$, and then the oxide PbO. The hydroxides of mercury and silver are evidently unstable, for, when the precipitate obtained by adding a soluble hydroxide to one of their soluble salts is dried, it is found to contain nothing but the corresponding oxide. With the exception of those of the metals of the alkalies and alkaline earths, the hydroxides are all little soluble in water.

Compounds of the Metals: Salts.—In the succeeding chapters we shall describe only those salts which are manufactured commercially, or are of special interest for some other reason. The various salts will be described under each metal. Here, however, a few remarks may be made about the characteristics of the more common groups of salts.

The **chlorides** may be made by the direct union of chlorine with the metal (see p. 180), or by the combined action of carbon and chlorine upon the oxide (see p. 449). The general methods for making any salt (p. 221), such as the interaction of a metal with an acid, or of the oxide, hydroxide, or another salt with an acid, or the double decomposition of two salts, may be used also for making chlorides. The chlorides are for the most part soluble in water. Silver chloride, mercurous chloride and cuprous chloride are almost insoluble, however, and lead chloride is not very soluble. Most of the chlorides of metals dissolve without appreciable decomposition, but hydrolysis is conspicuous in the case of the chlorides of the trivalent metals, such as aluminium chloride and ferric chloride (see p. 469). The chlorides of some of the bivalent metals (magnesium, calcium and zinc) are slightly hydrolyzed also, but, as a rule, only when they are heated with water. Most of the chlorides are stable when heated, but those of the noble metals, particularly gold and platinum, are decomposed, and chlorine escapes. The chlorides are usually the most volatile of the salts of a given metal. Some metals, for example iron, form two or more different chlorides.

The **sulphides** are formed by the direct union of the metal with sulphur, or by the action of hydrogen sulphide or of some soluble sulphide upon a solution of a salt (see p. 329). In one or two cases they are made by the reduction of the sulphate with

carbon. The sulphides, except those of the alkali metals, are but little soluble in water. The sulphides of aluminium and chromium are hydrolyzed completely by water, giving the hydroxides, and those of the alkali metals and the metals of the alkaline earths are partially hydrolyzed (see p. 330).

The **carbides** are usually formed in the electric furnace by interaction of an oxide with carbon (see p. 420). Some of them are decomposed by contact with water, after the manner of calcium carbide, giving a hydroxide and a hydrocarbon. Of this class are barium carbide BaC_2, aluminium carbide Al_4C_3, and manganese carbide MnC. Others, such as those of molybdenum Mo_2C and chromium Cr_3C_2, are not affected by water.

The **nitrates** may be made by any of the methods used for preparing salts. They are *all* at least fairly soluble in water.

The **sulphates** are made by the methods used for making salts, and in some cases by the oxidation of sulphides. They are all soluble in water, with the exception of those of lead, barium, and strontium. Calcium sulphate is meagerly soluble.

The **carbonates** are prepared by the methods used for making salts. They are all insoluble in water, with the exception of those of sodium and potassium. The hydroxides of aluminium and tin are so feebly basic that they do not form stable carbonates (see pp. 469-470).

The **phosphates** and **silicates** are prepared by the methods used in making salts. The former are obtained also by special processes already described (p. 412). With the exception of the salts of sodium and potassium, all the salts of both these classes are insoluble.

For the **exact solubilities** of a large number of **bases and salts** at 18°, see the **Table inside the cover**, at the front of this book. **Solubilities at other temperatures** are shown in the **diagram, Fig. 53**, p. 146.

Alloys. — In many cases metals dissolve in one another in the fused state, and when cooled form **alloys**. Alloys are of several types. In the first place, the metals may remain completely dissolved in one another in the solid state. An example is afforded by copper and manganese. A perfectly homogeneous

alloy, however, may also be obtained in other ways. If a liquid mixture is suddenly cooled ("quenched") it may exist indefinitely, like glass, in a super-cooled amorphous condition, being still, strictly speaking, a liquid. *Hard steel* (essentially a solution of about 1% carbon in iron) is an instance of this class. A third case in which a homogeneous alloy results is when exactly the necessary proportions of the two metals are taken to form a stable compound. Many such compounds are known, copper and magnesium for example giving the two compounds CuMg and Cu₂Mg, melting at 570° and 897° respectively.

The majority of alloys, nevertheless, although they may appear uniform to the eye, are heterogeneous in character, and when a polished surface is etched by a suitable chemical and examined under the microscope, the differences in crystal structure of the various components present are immediately evident. Most molten mixtures of metals deposit one component first on cooling, and only when the concentration of the other component has been considerably increased and the temperature considerably lowered does the second component begin to crystallize out as well. We thus obtain crystals of one metal imbedded in a matrix, or mother deposit, of another. If the metals are incompletely miscible in the solid state at low temperatures, or if metals that form compounds are taken in irregular proportions, substantially the same state of affairs is established.

In gray *cast iron* we have a very clear case of a heterogeneous alloy, tiny particles of carbon having separated out from the iron. *Babbitt's metal* (Sb 3, Zn 69, As 4, Pb 5, Sn 19 per cent) and other anti-friction alloys give, on cooling, a mass in general soft, but containing hard particles. The latter bear most of the pressure, yet, as the alloy wears, they are pressed into the softer matrix so that a smooth surface is always presented. An alloy with the opposite composition, a hard mass containing softer particles, would develop heat by friction much more rapidly.

The properties of alloys, especially when compounds are formed, may be markedly different from the properties of their constituent elements. Thus the nickel alloy used in coins contains 75 per cent of copper and only 25 per cent of nickel, yet it

shows none of the color of the former metal. The conductivity of *manganin* for electricity, on the scale used in the table on p. **468**, is only **2.3**, although it contains **84** per cent of copper to **4** of nickel and 12 of manganese. This alloy is used for wire resistances.

In subsequent chapters we shall take up many examples of alloys which are of great commercial value because of the elimination of certain very undesirable properties, or the introduction of certain highly desirable properties, which has resulted through the addition of a suitable proportion of one metal to another.

Alloys in which *mercury* is one of the components are known as **amalgams,** and are formed with especial ease by the lighter metals. Of the common metals, iron is the least miscible with mercury.

Exercises. — 1. What do we mean by saying that an oxide is strongly or feebly basic, or that it is acidic?

2. What is meant by the same terms when applied to an hydroxide?

3. Compare the molar solubilities at 18°, (*a*) of the halides of silver, and (*b*) of the carbonates and (*c*) oxalates of the metals of the alkaline earths, noting the relation between solubility and atomic weight.

4. What is the molar concentration of chloride-ion in saturated solutions of silver chloride and lead chloride at 18°, assuming complete ionization in these very dilute solutions?

5. Formulate, by means of ionic equations, the hydrolysis of ammonium sulphide $(NH_4)_2S$. Will a solution of this *neutral* salt exhibit an acid or an alkaline reaction (refer to table on p. 244)?

6. Why does not the precipitate of silicic acid obtained when ammonium silicate is dissolved in water re-dissolve when concentrated ammonia is added to the solution (compare p. 451)?

CHAPTER XXXIV

THE ALKALI METALS

THE metals of this family, with their atomic weights, are:

Lithium, Li	6.94	Rubidium, Rb		85.45
Sodium, Na	23.00	Cæsium, Cs		132.81
Potassium, K	39.10			

The Chemical Relations of the Alkali Metals. —Reference to the electromotive series of the metals (p. 240) will show that the metals which are chemically most active are included in this group. A freshly cut surface of any of these metals tarnishes by oxidation as soon as it is exposed to the air. All of these metals decompose water violently (see p. 59), liberating hydrogen. The hydroxides which are formed by this action are **alkalies** or exceedingly active bases (see p. 171). It is from this fact that the family receives its name. From the periodic classification of the elements (p. 358) it will be seen that the alkali metals all fall into place in the left hand side of the second column. In all their compounds they are **univalent.**

In this family, just as in the halogen family (p. 284), we shall find that although the elements and their corresponding compounds are all very much alike in properties, yet the first member is decidedly irregular in certain respects. Instead of beginning with lithium, therefore, we shall reverse the order of presentation, and start with the elements of higher atomic weight. **Caesium** and **rubidium** are both extremely rare elements, and their compounds have no particular interest. The first of the alkali metals to come up for discussion is consequently **potassium.**

POTASSIUM K

Occurrence. — Silicates containing potassium, such as felspar and mica (p. 453), are constant constituents of volcanic rocks. These minerals have not yet been brought into commercial use as sources of potassium compounds. Many salt deposits (see

below) contain potassium chloride, alone (sylvite) 'and in combination with other salts, and most of the compounds of potassium are manufactured from this material. Potassium sulphate occurs also in the salt layers.

Preparation. — Potassium was first made by Davy (1807) by bringing the wires from a battery in contact with a piece of moist potassium hydroxide. ' Globules of the metal appeared at the negative wire. Electrolytic processes have now come back into use, commercially, molten potassium chloride being the substance decomposed. Castner's reduction process involves the heating of potassium hydroxide with a spongy mass of carbide of iron. The potassium passes off as vapor, and is condensed:

$$6KOH + 2C \rightarrow 2K_2CO_3 + 3H_2 + 2K.$$
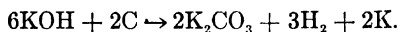
Physical and Chemical Properties. — Potassium is a silver-white metal (m.-p. 62°). It boils at 720°, giving a green vapor.

The density of the vapor shows the molecular weight of potassium to be about 40, so that the vapor is a monatomic gas. The element unites violently with the halogens, sulphur, and oxygen. In consequence of the latter fact it is usually kept under petroleum, an oil which neither contains oxygen itself, nor dissolves a sufficient amount of moisture from the air to permit much oxidation of the potassium to take place. A white, crystalline **hydride** KH is formed when hydrogen is passed over potassium heated to 360°. When thrown into water it gives potassium hydroxide, and the hydrogen is liberated.

Potassium Chloride KCl. — Sea-water and the waters of salt lakes contain a relatively small proportion of potassium compounds. During the evaporation of such waters, however, the potassium compounds tend to accumulate in the mother-liquor while sodium chloride is being deposited on the bottom. Hence the upper layers of salt deposits are the richest in compounds of potassium. Thus, at Stassfurt, near Magdeburg, there is a thickness of more than a thousand meters of common salt. Above this are 25–30 meters of salt layers in which the potassium salts are chiefly found.

The isolation of pure potassium chloride from the salt deposits will be taken up in a later chapter (p. 528), in connection with its use as a fertilizer. It is a white substance crystallizing in cubes, melting at about 750°, and slightly volatile at high temperatures.

The Other Halides of Potassium. — When iodine is heated in a concentrated solution of potassium hydroxide, potassium iodate and **potassium iodide** are both formed (compare p. 308):

$$6KOH + 3I_2 \rightarrow 5KI + KIO_3 + 3H_2O.$$

The dry residue from evaporation is heated with powdered carbon to reduce the iodate, and all the iodide can then be purified by recrystallization. The salt forms large, somewhat opaque cubes. It is used in medicine and for precipitating silver iodide AgI in photography (see p. 625).

The aqueous solution takes up free iodine, forming KI_3, in equilibrium with dissolved iodine: $I_3^- \rightleftarrows I^- + I_2$ (dissolved). It is used in testing for starch, and in reactions in which a solution of free iodine is required.

Potassium bromide KBr may be made in the same way as the iodide. It crystallizes in cubes. It is used in medicine and for precipitating silver bromide in making photographic plates.

The **fluoride of potassium** K_2F_2 may be obtained by treating the carbonate or hydroxide with hydrofluoric acid. It is a deliquescent, white salt. When treated with an equimolecular quantity of hydrofluoric acid it forms **potassium-hydrogen fluoride** KHF_2.

Potassium Hydroxide KOH. — This compound, known also as **caustic potash,** and colloquially as potassium hydrate, was formerly made entirely by boiling potassium carbonate with calcium hydroxide suspended in water (milk of lime):

$$\begin{array}{c} Ca(OH)_2(\text{solid}) \rightleftarrows Ca(OH)_2(\text{dslvd}) \rightleftarrows 2OH^- + Ca^{++} \\ K_2CO_3 \rightleftarrows 2K^+ + CO_3^= \end{array} \left.\right\} \rightleftarrows CaCO_3(\text{dslvd}) \rightleftarrows CaCO_3 \text{ (solid).}$$
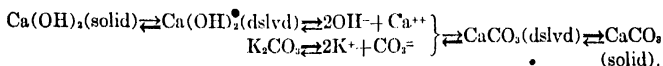
The operation is conducted in iron vessels, because porcelain, being composed of silicates, interacts with solutions of bases.

On account of the very limited solubility of the calcium hydroxide (0.08 g. in 100 g. water at 100°), the water takes up fresh portions into solution only when the part dissolved has already undergone chemical change. The calcium carbonate which is precipitated is, however, still more insoluble (0.0018 g. in 100 g. water), and hence the action goes forward. It cannot, nevertheless, for reasons which will be developed later (p. 571), be carried beyond a certain point, and in practice such an amount of water is employed that the solution at no time contains more than about 10 per cent of potassium hydroxide. The conclusion of the action is recognized when a clear sample of the liquid no longer effervesces on addition of a dilute acid, and is therefore free from potassium carbonate. After the precipitate has settled, the potassium hydroxide is obtained by evaporation of the clear liquid.

Potassium hydroxide is now manufactured by electrolytic processes also. Usually a solution of potassium chloride is electrolyzed, the details of the process being as already described for sodium hydroxide in an earlier chapter (p. 170).

Potassium hydroxide is exceedingly soluble in water, and consequently, instead of being crystallized from solution, the molten residue from evaporation is cast in sticks. The hydroxide is highly deliquescent. It also absorbs carbon dioxide from the air, giving potassium carbonate. Commercially, it is chiefly employed in the making of soft soap.

Potassium oxide K_2O may be made by heating potassium nitrate with potassium in a vessel from which air is excluded: $2KNO_3 + 10K \rightarrow 6K_2O + N_2$. It interacts violently with water, giving the hydroxide. When exposed to the air it unites spontaneously with oxygen, and a yellow **peroxide** K_2O_4 is formed. The same peroxide is formed when potassium burns in air or oxygen.

Potassium Chlorate $KClO_3$. — The preparation of this salt by interaction of potassium chloride with calcium chlorate has already been described (p. 308). It is also made by electrolysis of potassium chloride solution, the potassium hydroxide and chlorine which are liberated being precisely the materials re-

quired. All that is necessary is to use a warm, concentrated solution and to provide for the mixing of the materials generated at the electrodes. The salt crystallizes out when the solution cools.

Potassium chlorate crystallizes in monoclinic plates. It melts at 357°, and at a temperature slightly above this the visible liberation of oxygen begins (see pp. 31-33). On account of the ease with which its oxygen is liberated, the salt is employed in making fireworks and as a component of the heads of Swedish matches. It is also used in medicine.

The mode of preparing **potassium bromate** $KBrO_3$ and **potassium iodate** KIO_3 has already been described (p. 313).

Potassium Nitrate KNO_3. - - The supply of the natural nitrate being insufficient, the salt is made by double decomposition from Chile saltpeter $NaNO_3$:

$$NaNO_3 + KCl \rightarrow KNO_3 + NaCl \downarrow.$$
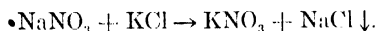
Sodium chloride is not much more soluble in hot water than in cold. The three other salts, however, become very soluble as the temperature rises (see Diagram, p. 146). Hence, when sodium nitrate and potassium chloride are heated with very little water, they dissolve, sodium chloride is precipitated, and potassium nitrate remains in solution. The mass is filtered quickly through canvas to separate the precipitate, and potassium nitrate crystallizes from the filtrate as it cools.

Potassium nitrate gives long prisms belonging to the rhombic system (Fig. 46, p. 105). It melts at about 340°, and when more strongly heated gives off oxygen, leaving potassium nitrite.

The salt is used in making gunpowder and fireworks. It is employed also in preserving ham and corned beef.

Gunpowder. --- Gunpowder is composed of potassium nitrate (75 per cent), charcoal (15 per cent) and sulphur (10 per cent). The ingredients are moistened with water, and intimately mixed by grinding under the heavy rollers of a mill. The "mill cake" is then broken up and granulated to the required size.

The explosion results largely from the union of the charcoal

with the oxygen from the nitrate, and of the sulphur with the potassium. One gram of powder yields 264 c.c. of gas (CO_2, CO, and N_2) measured at 0° and 760 mm., and a much larger volume at the temperature of the explosion. The chemical reactions involved produce, for each gram of the powder, about 660 calories of heat. The *explosion* is due to the *suddenness* with which the gases are generated and the heat is developed. The smoke is composed of particles of solid (hygroscopic) compounds of potassium and is therefore very slow in dissipating itself (see p. 338). **Smokeless powder** (p. 597) produces no solids when it explodes and has largely displaced gunpowder in recent years. The latter, however, is still extensively used in mining, and for detonating charges of smokeless powder."

Potassium Carbonate K_2CO_3. — This salt is manufactured chiefly from potassium chloride, from the Stassfurt deposits The chloride is heated with magnesium carbonate (magnesite), water, and carbon dioxide *under pressure:*

$$2KCl+3MgCO_3+CO_2+5H_2O\rightarrow2KHMg(CO_3)_2,4H_2O+MgCl_2.$$
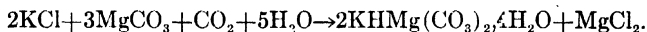
The hydrated mixed salt separates from the liquid containing the more soluble magnesium chloride and is decomposed by heating with water at 120°. The product is a solution of potassium carbonate, from which the precipitated magnesium carbonate is removed by filtration and used over again. In some districts potassium carbonate is still extracted from wood-ashes, its original source and the origin of its name, **potash.** The sugar beet takes up a considerable amount of potash from the soil, and the extract, after removal of the sugar, is evaporated and calcined. Wool scourings, when evaporated and calcined, also afford a small supply.

This salt is usually sold in the form of an anhydrous powder (m.-p. over 1000°). When crystallized from water it gives a hydrate $2K_2CO_3,3H_2O$. It is deliquescent. Its aqueous solution has a marked alkaline reaction. The commercial name of the substance is **pearl ash**. It is used in making soft soap and hard (*i.e.*, difficultly fusible) glass. It is also employed, by interaction with acids, in making other salts of potassium.

The use of the **bicarbonate** $KHCO_3$ in purifying carbon dioxide has already been mentioned (p. 422).

Potassium Cyanide KNC. — This salt, a derivative of the highly poisonous hydrocyanic acid (prussic acid) HNC, is made by heating dry potassium ferrocyanide (see p. 704):

$$K_4Fe(CN)_6 \rightarrow 4KNC + Fe + 2C + N_2.$$

When the residue is extracted with water, only the potassium cyanide dissolves, and it is easily crystallized in pure form from the solution.

Potassium cyanide is extremely soluble in water, and is therefore deliquescent. Its poisonous qualities are equal to those of hydrocyanic acid. A solution of the salt gives an alkaline reaction, showing that hydrocyanic acid is a feeble acid. It is so very feeble, indeed, as to be displaced by other weak acids like carbonic acid (compare p. 451). Hence, since the salt when exposed to the air is always moist, hydrocyanic acid is slowly liberated from it by the action of the carbon dioxide in the atmosphere. The salt consequently exhibits the bitter almond odor of the free acid. Potassium cyanide was formerly extensively used in electroplating (see p. 624), and in extracting gold (see p. 627) from its ores, but has been displaced by sodium cyanide NaNC, which is now less expensive.

Potassium Sulphate K₂SO₄. — Potassium sulphate is a constituent of several double salts found in the Stassfurt deposits. It is extracted from **schoenite** $MgSO_4,K_2SO_4,6H_2O$ and **kainite** $MgSO_4,MgCl_2,K_2SO_4,6H_2O$. The former is treated with potassium chloride and comparatively little water, whereupon the relatively insoluble potassium sulphate crystallizes out, and the magnesium chloride remains in the mother-liquor. The crystals belong to the rhombic system, contain no water of crystallization, and melt at 1066°. This salt is employed in preparing alum (see p. 584) and is much used as a **fertilizer**.

The methods of preparation and the properties of other salts of potassium in which sulphur is a constituent, such as the bisulphate, sulphide, sulphite, etc., have been given in sufficient detail in earlier chapters, to which reference should here be made.

Properties of Potassium-ion K^+: Analytical Reactions. — The positive ion common to all potassium salts is a colorless substance. It unites with all negative ions, and most of the resulting compounds are fairly soluble. For its **recognition** we add solutions containing those ions which give with it the least soluble salts. Thus, with chloroplatinic acid H_2PtCl_6 it gives a yellow precipitate of potassium chloroplatinate K_2PtCl_6. Since nearly one part of this salt dissolves in 100 parts of water, the test is far from being a delicate one. Picric acid (p. 598) gives potassium picrate $KC_6H_2(NO_2)_3O$, which is much less soluble in water (0.4 parts in 100 at $15°$). Perchloric acid and fluosilicic acid likewise give somewhat insoluble salts of potassium. **Potassium-hydrogen tartrate** $KHC_4H_4O_6$ is precipitated by the addition of tartaric acid to a sufficiently concentrated solution of a potassium salt. The neutral tartrate $K_2C_4H_4O_6$ is much more soluble. The latter may be obtained by treating the precipitate with a solution of potassium hydroxide. Addition of an acid to this solution causes reprecipitation of the bitartrate.

A much more delicate **test** for the recognition of a potassium compound consists in the examination by means of the **spectroscope** of the light given out by a Bunsen flame, in which a little of the salt is held upon a platinum wire. When the amount of potassium is considerable, and no other substance which would likewise color the flame is present to mask the effect, the violet tint is easily recognizable by the eye.

It may be noted in this connection that the two rare elements of the alkali group were named from the colors of the characteristic lines in their flame spectra, rubidium (red) and cæsium (blue). Rubidium is obtainable with relative ease from the mother-liquors of the Stassfurt works.

AMMONIUM

The compounds of ammonium claim a place with those of the alkali metals because in aqueous solution they give ammonium-ion NH_4^+, a substance which in its behavior closely resembles potassium-ion. Some of the special properties peculiar to ammonium compounds, and particularly the properties of ammo-

nium hydroxide NH_4OH, have been discussed in detail already (pp. 385-386).

Salts of Ammonium. —Ammonium chloride NH_4Cl, known commercially as **sal ammoniac**, is prepared from the ammonia dissolved by the water used to wash illuminating gas (p. 538), or that obtained from by-product coke ovens. It is purified by sublimation, and then forms a compact fibrous mass. At 337.8° its vapor exercises one atmosphere pressure, and is dissociated into ammonia and hydrogen chloride to the extent of 62 per cent (compare p. 386).

Ammonium nitrate NH_4NO_3 is a white crystalline salt which may be made by the interaction of ammonium hydroxide and nitric acid. When heated gently (m.-p. 166°) it decomposes, giving nitrous oxide and water (p. 400). It is used as an ingredient in fireworks and explosives.

When ammonium hydroxide is treated with excess of carbon dioxide the solution gives, on evaporation, **ammonium bicarbonate** NH_4HCO_3. This is a white crystalline salt which is fairly stable at the ordinary temperature. It has, however, a faint odor of ammonia, and its dissociation becomes very rapid when slight heat is applied. When a solution of this salt is treated with ammonium hydroxide, the **normal carbonate** $(NH_4)_2CO_3$ is formed. But this salt, when left in an open vessel, loses ammonia very rapidly, and leaves the bicarbonate behind.

Ammonium sulphate $(NH_4)_2SO_4$ is a white salt which is used chiefly as a fertilizer. By electrolysis of a concentrated solution of the **bisulphate** NH_4HSO_4, ammonium **persulphate** $(NH_4)_2S_2O_8$, which is less soluble, is formed and crystallizes out (see p. 349).

Solutions of **ammonium-hydrogen sulphide** NH_4HS and **ammonium sulphide**, $(NH_4)_2S$, made by passing hydrogen sulphide gas into ammonium hydroxide, are much used in analysis. The sulphide is almost completely hydrolyzed by water into the acid sulphide and ammonium hydroxide (compare sodium sulphide, pp. 324-326). It is used for the precipitation of sulphides, such as zinc sulphide ZnS, which are insoluble in water. Although the $S^=$ ions are not numerous at any moment, disturbance of the

equilibrium by their removal, when they pass into combination, causes displacements which result in the generation of a continuous supply.

The solutions, when pure, are colorless. They dissolve free sulphur, giving yellow polysulphides (p. 330). The same yellow substances are also obtained by gradual oxidation of ammonium sulphide, when the solution of this salt is allowed to stand in a bottle from which the air is imperfectly excluded.

Ammonium Amalgam. — When a salt of ammonium is decomposed by electrolysis the NH_4^+, upon its discharge, ordinarily gives ammonia and hydrogen, and no free NH_4 is obtained. If, however, a pool of mercury is used as the negative electrode, the NH_4 forms an amalgam with it, and there seems to be no doubt that this substance is actually present in solution in the mercury. While the amalgam is being formed it swells up and gives off the decomposition products above mentioned, so that the existence of the substance is only temporary. The same material may be obtained by putting sodium amalgam into a concentrated solution of a salt of ammonium. The action is a displacement of one ion by another (p. 240):

$$Na(\text{dissolved in Hg}) + NH_4^+ \rightarrow NH_4 \text{ (dissolved in Hg)} + Na^+.$$
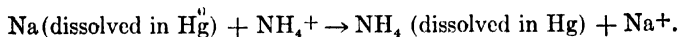
This behavior is interesting since it is in harmony with the idea that ammonium, if it could be isolated, would have the properties of a metal. Substances other than metals are not miscible with mercury.

Ammonium-ion NH_4^+: Analytical Reactions.—Ionic ammonium is a colorless substance. It unites with negative ions, giving salts, which, in the majority of cases, are soluble. Ammonium chloroplatinate $(NH_4)_2PtCl_6$, and to a less extent ammonium-hydrogen tartrate $NH_4HC_4H_4O_6$, are insoluble compounds, and their precipitation is used as a test. The surest means of recognizing ammonium compounds, however, consists in adding a soluble base to the substance (see p. 386). The ammonium hydroxide, which is thus formed, gives off ammonia, and the latter may be detected by its odor.

SODIUM Na

Occurrence. — Sodium chloride forms more than two-thirds of the solid matter dissolved in sea-water, and the great salt deposits are largely composed of it. Sea-plants contain mainly sodium salts of organic acids, just as land-plants contain potassium salts. Chile saltpeter and albite (a soda felspar) are important minerals.

Compounds of sodium are usually cheaper than the corresponding ones of potassium. Also, since the atomic weight of sodium is 23, against 39 for potassium, a smaller weight of the sodium compound will produce the same chemical result. For these two reasons, sodium compounds, except in special cases, are always preferred for commercial purposes.

Preparation. — Sodium was first made by Davy (1807) by electrolysis of moist sodium hydroxide. It is now manufactured by the electrolysis of fused sodium hydroxide by a method invented by Castner. The cathode C projects through the bottom of the iron vessel containing the fused hydroxide (Fig. 109), and is held in place by a cake S of solid sodium hydroxide in the lower part of the vessel. This electrode is surrounded by a wire-gauze partition to permit circulation of the fused mass, but prevent escape of the globules of sodium. It is
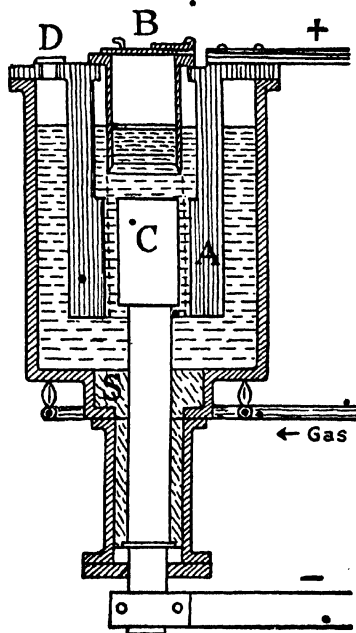
FIG. 109.

surmounted by a bell-shaped vessel of iron B, which floats in the fused alkali. In this the sodium and the hydrogen liberated at the cathode during the electrolysis collect. The atmosphere of hydrogen protects the fused metal from oxidation. The anode A is an iron cylinder surrounding the gauze and the oxygen collecting above it is allowed to escape through the vent D. The melted sodium is ladled out, from time t) time, into molds, like candle molds.

Properties. — Sodium is a soft, shining metal, melting at $96°$ and boiling at $742°$. The green vapor is a monatomic gas. The general chemical properties have already been given (p. 477). The metal unites with hydrogen to form a **hydride** NaH. Sodium is used in the manufacture of sodium peroxide and of many carbon compounds which are used as drugs and dyes. By contact action, it converts isoprene, an unsaturated hydrocarbon with the formula C_5H_8, into caoutchouc $(C_{10}H_{16})_n$ or raw rubber (see p. 590). This is a method of making rubber artificially. It cannot yet be carried out so cheaply as to compete with the natural product under ordinary circumstances, but in Germany during the war, when the supply of natural rubber was cut off entirely, considerable quantities were manufactured by this synthetic method.

   。 **Sodium Chloride NaCl.** — Common salt is obtained from the salt deposits of Stassfurt in Germany, in Cheshire (England), at Syracuse in New York, at Salina in Kansas, in Utah, California, and many other districts. Natural brines are obtained from wells in various parts of the world. Since the salt can seldom be used directly, on account of impurities which it contains, it is purified by recrystallization from water.ᵗ A certain amount is made, by evaporation, from sea water. The purest salt for chemical purposes is precipitated from a saturated solution of salt by leading into it hydrogen chloride gas. Explanation of this effect will be given presently (see pp. 569-571).

   Common salt crystallizes in cubes, which melt at $803°$. It is the source of all sodium compounds, with the exception of the nitrate. From it come also most of the chlorine and hydrogen

chloride used in commerce (see pp. 161, 175). It is a necessary article of diet, furnishing, for example, the hydrochloric acid in the gastric juice (p. 167).

The Hydroxide and Oxides. — Sodium hydroxide NaOH, called also, colloquially, **caustic soda**, is prepared by the action of slaked lime upon sodium carbonate, but mainly by the electrolysis of a solution of sodium chloride (p. 170). Its general chemical properties and uses have already been discussed (Chapter XII).

Sodium peroxide Na_2O_2 is made by heating sodium at 300–400° in air which has been freed from carbon dioxide. The sodium is placed on trays of aluminium, and is passed into the furnace against the current of air. In this way, the freshest sodium meets the air from which most of the oxygen has been removed, and the action is moderated. Conversely, the almost entirely oxidized sodium meets the freshest air, and completion of the oxidation is thus assured.

This oxide is the sodium salt of hydrogen peroxide. When thrown into water it decomposes in part, in consequence of the heat developed, giving sodium hydroxide and oxygen. With careful cooling, however, much of it can be dissolved unchanged. By interaction with acids it yields hydrogen peroxide (p. 290). Sodium peroxide is now used commercially for oxidizing and bleaching, and, in the form of oxone (p. 32), as a source of oxygen. The ordinary **sodium oxide** Na_2O is made in the same way as is potassium oxide (p. 480).

The Nitrate. — The occurrence of **sodium nitrate** $NaNO_3$ and its use in the manufacture of nitric acid have already been described (p. 388). Its crystals are rhombohedral. This salt is one of the best of fertilizers (see p. 526). It is used also in the manufacture of potassium nitrate (p. 481).

Sodium Carbonate. — Natural sodium carbonate is found in Egypt and in other parts of the world. At Owen's Lake, California, it is secured by solar evaporation of the water. The sesquicarbonate $Na_2CO_3,NaHCO_3,2H_2O$, being the least soluble of the carbonates of sodium, is the one deposited. Locally, small quantities of sodium carbonate are still made by the burning of

seaweed. The substance is manufactured from sodium chloride in two ways, namely by the Le Blanc process and by the Solvay process.

The **Le Blanc process** (1791) involves three chemical actions. In the first place, sodium chloride is treated with an equivalent amount of sulphuric acid in a large cast-iron or earthenware pan. The bisulphate thus produced (see p. 532), together with the unchanged sodium chloride, is raked out into a rotating, inclined iron cylinder, and heated more strongly until the action is completed:

$$NaCl + NaHSO_4 \rightleftarrows Na_2SO_4 + HCl \uparrow .$$
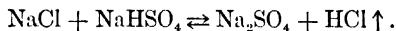
The product of this treatment is called **salt cake**. The hydrogen chloride, which is liberated in both stages, passes through towers containing running water in which it is absorbed. The second and third actions which follow are conducted in one operation. They consist in the reduction of the sodium sulphate by means of powdered coal and the interaction of the resulting sulphide of sodium with chalk or powdered limestone, leaving finally **black ash**:

$$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2,$$
$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS.$$
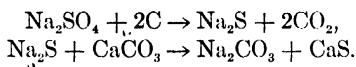
Calcium sulphide is not very soluble in water, and is consequently but slowly hydrolyzed by it (p. 330), especially when calcium hydroxide is present. The sodium carbonate is therefore extracted from the black ash by a systematic treatment of the ash with water. The ash is placed in a series of vessels at different levels, and a stream of water (30–40°) flows from one vessel to another, until, when it issues from the last, it is completely saturated with sodium carbonate. When the material in the first of the vessels has been exhausted, the water is allowed to enter the second vessel directly, and a vessel containing fresh black ash is added at the lower end of the series. In this way the most nearly exhausted ash comes in contact with pure water, which is in the best position to dissolve the remaining sodium carbonate rapidly, while the fresh black ash encounters a solution already almost at the point of saturation. The commercial survival of the process depends upon the recovery of the

sulphur from the spent black ash, and of the hydrogen chloride.

The **Solvay, or ammonia-soda process** (1860), has now displaced the Le Blanc process almost entirely. It differs from the latter by involving almost nothing but ionic actions. A solution of salt, saturated with ammonia and warmed to 40°, fills a tower divided by a number of perforated partitions. Carbon dioxide, made by heating limestone in special kilns, is forced in at the bottom. The perforations split up the gas into small bubbles, and facilitate its solution to form carbonic acid H_2CO_3. With the ammonium hydroxide NH_4OH in the liquid this gives ammonium bicarbonate:

$$NH_4OH + H_2CO_3 \rightleftarrows NH_4HCO_3 + H_2O.$$
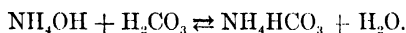
The ammonium bicarbonate now interacts by double decomposition with the sodium chloride, and sodium bicarbonate, which is a much less soluble salt, is precipitated:

$$NaCl + NH_4HCO_3 \leftrightarrows NaHCO_3 \downarrow + NH_4Cl.$$
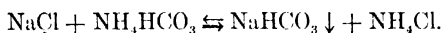
The solid sodium bicarbonate, after being freed from the liquid by filter-presses, is heated strongly and leaves behind sodium carbonate:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O \uparrow + CO_2 \uparrow.$$
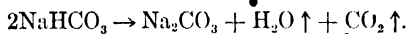
The carbon dioxide which is liberated passes through the operation once more. The mother-liquor from the sodium bicarbonate contains ammonium chloride. This is decomposed by heating with quicklime from the kilns, and the ammonia which is thus obtained is available for the treatment of another batch.

The anhydrous sodium carbonate **(soda ash or calcined soda)** is recrystallized from water, giving the decahydrate Na_2CO_3, **$10H_2O$, soda crystals, or washing soda.** The bicarbonate is **baking soda.**

Properties of the Carbonate and Bicarbonate. — The **decahydrate** $Na_2CO_3,10H_2O$ has a fairly high aqueous tension, and loses nine of the ten molecules of water which it contains when it is exposed in an open vessel (p. 85), leaving the monohydrate. At higher temperatures, or in a dry atmosphere (p. 84), this in turn can be completely dehydrated. In aqueous solution,

sodium carbonate is appreciably hydrolyzed (2.3 per cent in $0.1N$ solution at $25°$), and shows a marked alkaline reaction (p. 424). The compound is used in large amounts for the manufacture of glass and soap, and in the softening of water, and is applied in innumerable ways in the scientific industries for purposes akin to cleansing.

Sodium bicarbonate $NaHCO_3$ can be prepared in a state of purity by passing carbon dioxide over the decahydrate of sodium carbonate:

$$Na_2CO_3,10H_2O + CO_2 \rightleftarrows 2NaHCO_3 + 9H_2O.$$
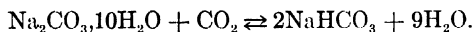
This action is reversible (compare p. 425), and sodium bicarbonate shows, even in the cold, an appreciable tension of carbon dioxide. The aqueous solution of the *pure* substance is faintly alkaline (see p. 424). The salt is used in the manufacture of baking powder and in medicine.

Other Salts of Sodium.—Anhydrous sodium sulphate Na_2SO_4 (thenardite) is found in the salt layers. The same salt is contained in mineral waters, such as those of Karlsbad. It is used, as a substitute for sodium carbonate, in making inexpensive glass.

The **decahydrate** $Na_2SO_4,10H_2O$ **(Glauber's salt)** forms large monoclinic crystals which give up all their water of hydration when kept in an open vessel. For the solubilities of the hydrate and anhydrous substance, see Fig. 54 (p. 150).

Sodium thiosulphate $Na_2S_2O_3,5H_2O$ is made by boiling a solution of sodium sulphite with sulphur (p. 348). A standard solution (p. 261) of the thiosulphate is used in determining quantities of free iodine:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$
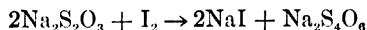
Colorless **sodium tetrathionate** is formed, and the "end point" (consumption of all the iodine) can be ascertained by the starch test (see p. 276).

When heated, dry sodium thiosulphate decomposes, giving sodium sulphate, which is the most stable oxygen-sulphur compound of sodium (see p. 335), and sodium pentasulphide:

$$.4Na_2S_2O_3 \rightarrow 3Na_2SO_4 + Na_2S_5.$$

From the latter, four unit-weights of sulphur can be driven by stronger heating. Sodium thiosulphate is used for fixing negatives in photography (see p. 625), and by bleachers as an antichlor (p. 297).

Sodium hyposulphite $Na_2S_2O_4$ is prepared in solution by the action of zinc on sodium bisulphite and excess of sulphurous acid:

$$Zn + 2NaHSO_3 + H_2SO_3 \rightarrow Na_2S_2O_4 + ZnSO_3 + 2H_2O.$$
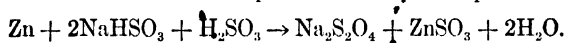
The solution is an active reducing agent, and is employed largely by dyers, for example in reducing indigo (insoluble) to indigo white (soluble in an alkaline liquid), in preparing the vat of dye.

Common sodium phosphate is a dodecahydrate of the secondary orthophosphate, $Na_2HPO_4,12H_2O$. It is made by neutralization of phosphoric acid with sodium carbonate. Its properties have already been discussed (p. 412).

Sodium tetraborate $Na_2B_4O_7,10H_2O$ (borax) has also been discussed under boron (p. 456). It is used as an ingredient in glazes for porcelain, in soldering, for bead reactions (p. 456) and for preserving food.

Sodium disilicate $Na_2Si_2O_5$ (see p. 451) is used for fireproofing wood and other materials, and for preserving eggs. Sand which is moistened with it and pressed in molds, forms, after baking, a serviceable artificial stone.

Properties of Sodium-ion Na^+: Analytical Reactions. — Sodium-ion is a colorless ionic material which unites with all negative ions. Practically all the salts so formed are soluble in water. The only ones which can be precipitated from dilute solution are sodium fluosilicate Na_2SiF_6, made by the addition of fluosilicic acid to a concentrated solution of a sodium salt, and sodium-hydrogen pyroantimoniate $Na_2H_2Sb_2O_7$, made by similar addition of the corresponding potassium salt. All compounds of sodium confer a yellow color on the Bunsen flame, but this test is so delicate that it is shown by the traces of sodium contained in almost all substances.

Lithium. — Lithium occurs in lepidolite (a lithia mica), in amblygonite, and in other rare minerals. Traces of compounds of the element are found widely diffused in the soil, and are

taken up by plants, particularly tobacco and beets, in the ashes of which the element may be detected spectroscopically.

The metal is liberated by electrolysis of the fused chloride. The specific gravity of the free element (0.53) is lower than that of any other metal. Lithium not only floats upon water, but also in the petroleum in which it is preserved.

The metal behaves towards water and oxygen like sodium (p. 59). It unites directly and vigorously with hydrogen (LiH), nitrogen (Li_3N), and oxygen (Li_2O), forming stable compounds. In the fused state the hydride is a conductor of electricity, positive lithium-ion Li^+ travelling to the cathode and **negative hydride-ion** H^- (see p. 364) going to the anode. The relative insolubility (see Table on inside front cover) of the hydroxide LiOH, the carbonate Li_2CO_3, and the phosphate $Li_3PO_4,2H_2O$ is in sharp contrast to the easy solubility of the corresponding compounds of the other alkali-metals, and links lithium with magnesium. The compounds of lithium give a bright-red color to the Bunsen flame. The carbonate is used in medicine.

Exercises. — 1. The vapor density of sodium peroxide has not been determined. Why is the formula Na_2O_2 assigned to it?

2. Construct a scheme of equilibria (p. 330) showing the hydrolysis of calcium sulphide. Why does the presence of calcium hydroxide diminish the tendency to hydrolysis (p. 209)?

, 3. Why should a mixture of potassium chlorate and antimony trisulphide be explosive?

4. How should you set about making, (*a*) a borate of potassium, (*b*) potassium pyrophosphate, (*c*) ammonium nitrite, (*d*) ammonium chlorate, (*e*) ammonium iodide?

5. In the Solvay process why is the ammonia dissolved in the salt solution, and not separately in water? Make the equation for the action of heat on limestone.

⁀6. What is the exact percentage of water in washing soda?

7. Write full ionic equations for the Solvay process (p. 491).

8. Why does a solution of ammonium sulphide $(NH_4)_2S$ smell of ammonia and hydrogen sulphide?

CHAPTER XXXV

THE ALKALINE EARTH METALS

The Chemical Relations of the Elements. — The familiar metals of this group, calcium (Ca, at. wt. 40.07), strontium (Sr, at. wt. 87.63), and barium (Ba, at. wt. 137.37), constitute a typical chemical family, both in the qualitative resemblance to one another of the elements and of the corresponding compounds, and in the quantitative variation in the properties with increasing atomic weight. In the electromotive series of the metals (p. 240), the members of this group fall just below the alkali metals. The metals themselves displace hydrogen vigorously from cold water, giving hydroxides. The solutions of these hydroxides, although dilute, on account of a rather small solubility, are strongly alkaline in reaction. The high degree of ionization of the hydroxides recalls the hydroxides of the metals of the alkalies, and their relative insolubility the hydroxides of aluminium and the "earths" (Chapter XLI).

In all their compounds, calcium, strontium, and barium are **bivalent**, in correspondence with their position in the periodic system (p. 358). The hydroxides are formed by union of the oxides with water, and are progressively less easy to decompose by heating, barium hydroxide being the hardest. The carbonates, when heated, yield the oxide of the metal and carbon dioxide, barium carbonate being the most difficult to decompose. The nitrates, when heated moderately, give the nitrites, but the latter are broken up by further heating and yield the oxide of the metal, and nitrogen tetroxide. In these and other respects the compounds of the metals of the alkaline earths resemble those of the heavy metals and differ from those of the metals of the alkalies. Barium approaches the latter most nearly.

The table of solubilities (inside front cover) shows that the chlorides and nitrates of calcium, strontium, and barium are all soluble in water, the solubility diminishing in the order given.

The sulphates and hydroxides cover a wide range from slight solubility to extreme insolubility. Of the sulphates, 2000, 110, and 2.3 parts, respectively, dissolve in one million parts of water at 18°. In the case of the hydroxides the order of magnitude is reversed, and the corresponding numbers are 200, 630, and 2200. The carbonates are almost as insoluble as is barium sulphate.

· CALCIUM Ca ·

Occurrence. — The fluoride, and the various forms of the carbonate, sulphate, and phosphate, which are found in nature, are described below. As silicate, calcium occurs, along with other metals, in many minerals and rocks. Compounds of the element are found also in plants, and in the bones and shells of animals.

Calcium. — The metal is made by electrolyzing melted calcium chloride in a graphite crucible, which forms the anode. The cathode is a rod of iron, one end of which dips into the fused salt. The calcium, liberated at this point, adheres to the rod. The latter is slowly raised, in such a way that the calcium always remains in contact with the liquid. In this fashion a long "cabbage-stalk" of calcium is finally produced.

Calcium is a silver-white, crystalline metal (m.-p. 800°, sp. gr. 1.55) which is a little harder than lead, and can be cut, drawn, and rolled. It burns in the air, giving a mixture of the oxide and **nitride** Ca_3N_2 (compare p. 367).

A white crystalline **hydride** CaH_2 is formed by direct union with hydrogen. It is known in commerce as **hydrolyte.** It is an expensive, but portable source of hydrogen for filling war balloons:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2.$$
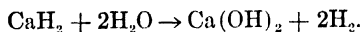
Calcium Chloride $CaCl_2$. — This salt, for which there is no extensive commercial application, is formed as a by-product in many industrial operations. Thus, it is a by-product of the Solvay soda process (p. 491). By concentrating and cooling its aqueous solution, the **hexahydrate** $CaCl_2,6H_2O$ is obtained below 30° in large, deliquescent, six-sided prisms. On account of the great concentration of a saturated solution of this compound,

the solid and solution do not reach a condition of equilibrium with ice (see p. 155) until the temperature has fallen below − 50°. The Solvay process brine (p. 491), when mixed with ice, gives, therefore, a very efficient freezing mixture. On account of its deliquescent character, the solid salt is sprinkled on roads to lay the dust.

Calcium chloride, partly dehydrated by heating, $CaCl_2,2H_2O$, forms a porous mass which is used in chemical laboratories for drying gases and liquids. When complete dehydration is attempted, the salt interacts with the water, giving some calcium oxide.

Calcium chloride forms compounds, not only with water, but also with ammonia ($CaCl_2,8NH_3$) and with alcohol. For drying these substances, therefore, quicklime is employed.

Calcium Fluoride CaF_2. — This compound occurs in nature as fluorite or fluor-spar CaF_2. It crystallizes in cubes, is insoluble in water, and when pure is colorless. Natural specimens often possess a green tint or show a violet fluorescence. It is formed as a precipitate when a soluble fluoride is added to a solution of a salt of calcium.

Fluorite is used in the etching of glass, as the source of the hydrogen fluoride (p. 283). It is easily fusible, as its name indicates (Latin, *fluere*, to flow), and is employed in metallurgical operations as a flux (p. 471).

Calcium Carbonate $CaCO_3$. — The carbonate is the commonest compound of calcium. White **marble** is a pure variety, composed of crystals compactly **wedged** together. **Limestone** does not show much crystalline structure and usually contains clay and other impurities. **Chalk** is made up of shells of minute marine organisms. **Shells, coral,** and **pearls** are likewise mainly calcium carbonate. **Well-formed** crystals (**calcite,** or Iceland spar — Fig. 110 — and **aragonite** — Fig. 111) are common.
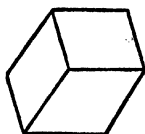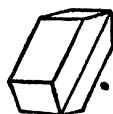
Fig. 110.

Fig. 111.

When heated, calcium carbonate dissociates, giving carbon dioxide and quicklime:

$$CaCO_3 \rightleftarrows CaO + CO_2.$$
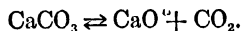
At ordinary temperatures the decomposition is imperceptible. On the contrary, atmospheric carbon dioxide, in spite of its very low partial pressure, combines with quicklime, giving "air-slaked" lime. As the temperature rises, however, **the tension of**
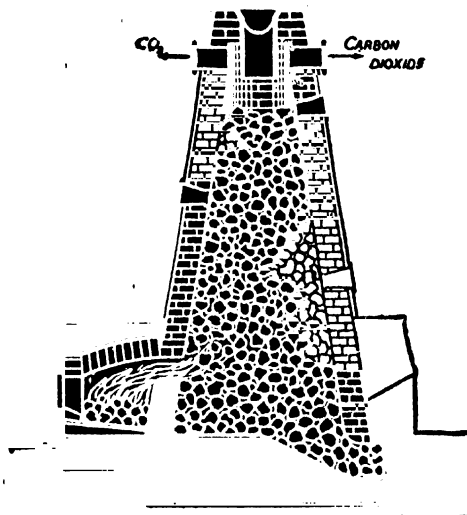
Fig. 112.

carbon dioxide coming from the carbonate increases, and **has a fixed value for each temperature.** If it is continuously allowed to escape, so that the maximum pressure is not reached, the whole of the salt eventually decomposes. At 700° the pressure is only 25' mm., at 900° it reaches an atmosphere, and at 950° two atmospheres. The phenomenon is precisely similar to the dissociation of a hydrate (p. 85).

Limestone is soluble in water containing carbonic acid, giving calcium bicarbonate (p. 425, also see p. 501). By solution of limestone, caves are often formed. Conversely, subterranean

water containing the bicarbonate, when it reaches such a cavern, loses carbon dioxide and deposits calcium carbonate as stalactites or columns hanging from the ceiling. The drippings form stalagmites on the floors.

Limestone is used in the manufacture of quicklime and of glass. It is employed largely as a flux in metallurgy, when minerals rich in silica are brought into fusible form by the production of calcium silicate $CaSiO_3$. Large amounts also find application as building-stone.

Calcium Oxide and Hydroxide. — Pure oxide of calcium CaO (quicklime) may be made by ignition of pure marble or calcite. For commercial purposes limestone is converted into quicklime in kilns (Fig. 112). The flames and heated gases from the fire pass between the pieces of limestone, and the carbon dioxide liberated is carried off by the draft. When the gas is to be used in the Solvay process or in the refining of sugar, coke (smokeless), instead of coal, is employed as the fuel. As low a temperature as possible is used. A high temperature causes impurities in the limestone (e.g., clay) to interact with the quicklime, giving fusible silicates, which fill the pores and interfere with the subsequent slaking with water. Since the change is reversible, if the gas lingers in the kiln (at 760 mm. pressure), a temperature over 900° is required to drive the action forward (p. 498). However, a good draft, which removes the gas as fast as it is formed, permits the use of a lower temperature.

Pure calcium oxide is a white, porous solid. It is barely fusible in the oxyhydrogen flame, but may be melted and boiled in the electric arc. It is not reducible by sodium, or by carbon excepting at the temperature of the electric furnace.

When water is poured upon quicklime, it forms **calcium hydroxide** $Ca(OH)_2$:

$$CaO + H_2O \leftrightarrows Ca(OH)_2.$$
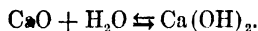
The product is a bulky powder. Much heat is evolved, and part of the water is turned into steam. The change is reversible, and at a high temperature the hydroxide can be dehydrated.

Calcium hydroxide is slightly soluble in water, and the solubility decreases with rising temperature (see p. 147). On account of its cheapness, this substance is used by manufacturers in almost all operations requiring a base, and it thus occupies the same position amongst bases that sulphuric acid does amongst acids. Caustic lime is employed in the manufacture of alkalies (p. 479), bleaching powder, and mortar (see below), the purification of sugar (p. 518), the removal of the hair from hides in preparation for tanning, the softening of water (see below) and as a whitewash.

Mortar. — Mortar is made by mixing slaked lime with three or four times its bulk of sand, and making the whole into a paste with water. When the water evaporates, a porous, rather crumbly material remains. This, however, at once begins to harden, owing to the action of the carbon dioxide in the air upon the lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \uparrow.$$
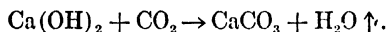
The crystalline calcite ($CaCO_3$) adheres to, and is interlaced with, the sand, and gives a rigid, though porous, structure attached firmly to the brick or stone. The pores facilitate the penetration of the air into the deeper parts and thus provide, both for the fresh supplies of carbon dioxide required for the continuance of the action shown in the equation, and for a considerable amount of useful ventilation through walls of the building.

Calcium Sulphate CaSO₄. — Calcium sulphate is a very common mineral. It occurs, as **anhydrite** $CaSO_4$, in salt deposits. **Gypsum** $CaSO_4,2H_2O$ is found in masses, and also in single crystals (selenite, Fig. 47, p. 105). **Alabaster** is highly crystalline gypsum, tinted by impurities.

Gypsum $CaSO_4,2H_2O$ is the commonest form, and is the one produced when calcium sulphate is precipitated. It is white and much softer than calcite. It is only slightly soluble in water (1 : 500 at 18°). It is used as a fertilizer and in making plaster of Paris and is the chief component of blackboard crayon or "chalk,"

When gypsum is heated, the vapor pressure of the water it gives off soon exceeds that of the moisture in the atmosphere, and the compound begins to decompose:

$$2[CaSO_4,2H_2O] \rightleftarrows (CaSO_4)_2,H_2O + 3H_2O \uparrow.$$

The hemi-hydrate which remains **(plaster of Paris)** gives a much lower pressure of water vapor and is more stable. Plaster of Paris is manufactured in large quantities by heating gypsum in kilns. When moistened with water, it sets in about half an hour to a solid mass of gypsum. The temperature used in making it must not exceed 125°, otherwise the hemi-hydrate is itself decomposed, the plaster is "dead burnt," and it no longer sets readily. The setting involves, simply, the reversal of the equation given above.

Plaster of Paris swells somewhat, in setting, and so fills out completely every detail of a mould and applies itself closely to the outline of an object on which it is spread. It is used in making casts, and in surgical bandages where movable parts are to be held rigidly in place. **Stucco** is made with sizing or glue instead of pure water.

Casts are made smooth and non-porous ("ivory" surface) by a coating of paraffin which fills the pores. Excellent imitations of bronze or other castings are produced by rubbing with pulverized metals.

What Makes Water Hard. — All natural waters except rain water, which is "soft," contain salts of calcium and magnesium in solution and are more or less "hard." These salts are dissolved by the water in its passage over and through the soil.

Although limestone is very insoluble in pure water (0.013 g. per liter), yet it interacts with the carbonic acid contained in all natural waters, giving **calcium bicarbonate** which is about thirty times more soluble under atmospheric conditions:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 + CaCO_3 \rightleftarrows Ca(HCO_3)_2.$$

When the water is boiled, these actions are all reversed. The carbon dioxide is driven out of solution, the carbonic acid is decomposed, and the calcium bicarbonate gives calcium carbonate, most of which is at once precipitated. Iron carbonate is

also held in solution as bicarbonate $Fe(HCO_3)_2$ and is precipitated 'as $FeCO_3$ by boiling. These two bicarbonates constitute **temporary hardness**. Their decomposition causes the "fur" in a kettle.

The sulphates of calcium (solubility 2 g. per liter) and of magnesium (very soluble) are also commonly 'found in natural waters. These salts are not altered by boiling and, along with magnesium carbonate (sol'ty 1 g. per l.)' and calcium carbonate (sol'ty 0.013 g. per l.), give **permanent hardness** to the water.

Consequences of Hardness in Water. — When hard water is used in a steam boiler, the salts, of course, are not carried off with the steam, but accumulate amazingly as fresh water is injected and steam alone is drawn off. In time, heavy deposits of *boiler crust* settle on the tubes of the boiler, and interfere with the transference of heat from the metal to the water. One-fourth of an inch of crust will increase the bill for fuel by 50 per cent. In addition to this the iron is heated to a higher temperature and may even become red hot. In consequence, it combines more rapidly with oxygen on the outside and displaces hydrogen from the water (p. 60) on the inside, giving in both cases Fe_3O_4 Thus the life of the boiler is shortened. If the formation of the crust is not prevented, or if the crust is not removed, the boiler may explode and great damage may be done.

When hard water is used for *washing*, in the *household* or *laundry*, much soap has to be dissolved before the necessary lather can be secured. Soap, which consists of a mixture of the sodium salts of several organic acids, such as palmitic acid $H.CO_2C_{15}H_{31}$ (see p. 545), interacts by double decomposition with the salts of calcium and magnesium giving palmitates, etc., of these metals. These salts are insoluble and form a "curd." With sodium palmitate $Na(CO_2C_{15}H_{31})$, for example, the action is

$$CaSO_4 + 2Na(CO_2C_{15}H_{31}) \rightarrow Ca(CO_2C_{15}H_{31})_2 \downarrow + Na_2SO_4.$$
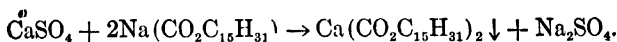
Not until all the salts causing the hardness have been decomposed does the permanent solution of soap which is required for washing begin to be formed. The waste thus involved is often very great and expensive.

Treatment of Hard Water. — *Temporary* hardness is commonly removed, on a large scale, by adding *slaked lime* in *exactly the quantity* shown by an analysis of the water to be required, and stirring for a considerable time:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O. \qquad (1)$$
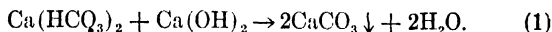
The bicarbonate is neutralized and the carbonate which is precipitated is removed by filtration.

Permanent hardness is not affected by slaked lime, but is removed by adding sodium carbonate in the necessary proportion:

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4. \qquad (2)$$

When *both kinds of hardness* are present, crude caustic soda (sodium hydroxide) may be employed. It neutralizes the bicarbonate, precipitating $CaCO_3$:

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3 \downarrow + Na_2CO_3 + 2H_2O \qquad (3)$$

and giving sodium carbonate. The latter then acts as in equation (2).

Instead of this, the treatments indicated in equations (1) and (2) may be applied in combination (Porter-Clark process).

In the new **permutite process** the water is simply filtered through an artificial sodium silico-aluminate (permutite) which is supplied in the form of a coarse sand. The calcium, etc., in the water is exchanged for sodium, which does no harm. If we use for permutite the abbreviated formula $Na\overline{P}$, we may write the reaction thus:

$$Ca(HCO_3)_2 + 2Na\overline{P} \rightarrow 2NaHCO_3 + Ca\overline{P}_2.$$
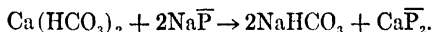
After twelve hours' use, the permutite is covered with 10 per cent salt solution and allowed to remain for the other twelve hours of the day, when it is ready for employment once more:

$$2NaCl + Ca\overline{P}_2 \rightarrow CaCl_2 + 2Na\overline{P}.$$
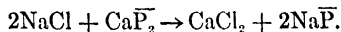
Only salt, which is inexpensive, is consumed, and calcium chloride solution is thrown away. Permutite removes magnesium, iron, manganese, and other elements in the same way. The life of a charge is said to be over twenty years.

Hard Water in the Laundry. — As we have seen (p. 502), soap will soften water, but the calcium and magnesium salts of the soap acids, which are precipitated, are sticky, and soil the goods being washed. Other substances that soften water not only give non-adhesive precipitates, but are also much cheaper, and an attempt is generally made to utilize them. The use of slaked lime is impracticable on a small scale.

Washing soda $Na_2CO_3,10H_2O$ is added to precipitate both kinds of hardness:

$$Ca(HCO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2NaHCO_3$$
$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4.$$
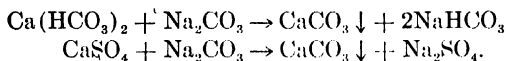
The small amounts of salts of sodium which remain in the water have no action on soap.

Household Ammonia NH_4OH acts like sodium hydroxide (p. 503):

$$Ca(HCO_3)_2 + 2NH_4OH \rightarrow CaCO_3 \downarrow + (NH_4)_2CO_3 + 2H_2O$$
$$CaSO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 \downarrow + (NH_4)_2SO_4$$
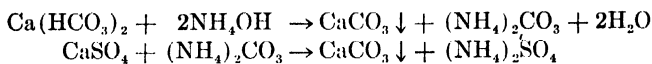
except that it will *not* precipitate magnesium-ion (see p. 560).

When *borax* $Na_2B_4O_7,10H_2O$ (p. 456) is added, it is hydrolyzed and the sodium hydroxide contained in its solution acts as already described.

The supposed bleaching or whitening action of borax or soda is a myth; these salts *prevent staining by the iron* in the water. They simply precipitate the iron (present as $Fe(HCO_3)_2$), which almost all waters contain, as $FeCO_3$ *before* the goods are put in. This precipitate is easily washed out in rinsing. The palmitate, etc., of iron, however, which the soap itself would throw down, is sticky and adheres to the cloth. The air subsequently oxidizes it and gives hydrated ferric oxide (rust), which is brownish-red.

It is evident that, properly to achieve their purpose, the soda and borax must be added, must be completely dissolved, and must be allowed to produce the precipitation of $FeCO_3$, $CaCO_3$, etc., all *before* the soap, or the goods, is introduced. If the soap is dissolved before or with the soda, *it* will take part in the precipitation, and give sticky particles containing the iron and calcium salts of the soap acids.

Other Salts of Calcium. — **Bleaching-powder** $CaCl(OCl)$ (p. 296), calcium **bisulphite** (p. 335), and the **phosphates** of calcium (p. 527) are elsewhere discussed. The hydrolysis of calcium **sulphide** in solution has also been mentioned previously (p. 330). A solution of this salt is used as a depilatory, since the proteins contained in hair and wool are decomposed by, and dissolved in alkaline solutions, like that here formed.

Ordinary calcium sulphide, after it has been exposed to sunlight, usually shines in the dark. Barium sulphide behaves in the same way. On this account these substances are used in making **luminous paint.** They apparently owe this behavior to the presence of traces of compounds of vanadium and bismuth, for the purified substances are not affected in the same fashion.

The use of calcium **silicate** $CaSiO_3$ in glass manufacture has already been described.

Calcium **oxalate** CaC_2O_4 may be observed under the microscope in the cells of many plants. Since it is the least soluble common salt of calcium, its formation by precipitation is used as a **test** for calcium ions.

The manufacture of calcium **carbide** CaC_2 in the electric furnace has been taken up in an earlier chapter (p. 421).

Calcium Cyanamide $CaCN_2$. — Calcium carbide, when strongly heated, absorbs nitrogen, giving a mixture of calcium cyanamide and carbon (**nitro-lime**):

Fig. 113.

$$CaC_2 + N_2 \rightarrow CaCN_2 + C.$$
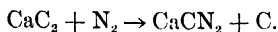
The carbide is pulverized and placed in a cylindrical furnace (Fig. 113), holding 300 to 450 kg. The heat (800 to 1000°) is furnished by the passage of a current of electricity through a thin carbon rod, which passes through the
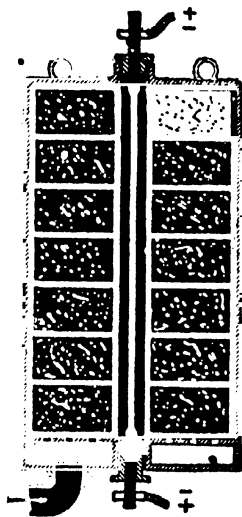
axis. The tube surrounding the rod and the other partitions are of cardboard, which burns up and leaves openings for the circulation of the nitrogen. The latter is made by the fractionation of liquid air and is introduced under pressure. In thirty-five hours nitrogen ceases to be absorbed, and the product is pulverized when cold.

Calcium cyanamide is now manufactured in large quantities at Niagara Falls (Ontario) and Odda (Norway) for use as a **fertilizer.** It is also a valuable source of ammonia, and was utilized very extensively as such for the manufacture of **explosives** during the Great War. When treated with hot water, calcium cyanamide is decomposed as follows:

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3. \quad .$$

In practice, pulverized nitro-lime is fed into an autoclave charged with water. Impurities such as free calcium carbide and calcium phosphide are immediately decomposed, and the gases evolved allowed to escape. Small amounts of alkali are then added to facilitate the evolution of ammonia and to prevent the formation of complex nitrogen compounds. The autoclave is closed and steam admitted until the pressure rises to 3–4 atmospheres, the heat evolved by the decomposition of the cyanamide being sufficient to carry the reaction to rapid completion. The ammonia given off is absorbed in water, or converted directly to ammonium sulphate. When the gas ceases to be given off, steam is blown through the liquor in the autoclave until all residual dissolved ammonia is expelled.

The productive capacity of cyanamide plants in 1920 exceeded 1,750,000 tons, calculated as nitro-lime.

Nitro-lime, when fused with sodium carbonate, gives **sodium cyanide** NaNC, used in the extraction of gold (p. 627):

$$CaCN_2 + C + Na_2CO_3 \rightarrow CaCO_3 + 2NaNC.$$
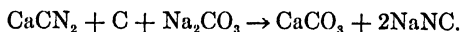
Calcium-ion Ca++: Analytical Reactions. — Ionic calcium is colorless. It is bivalent, and combines with negative ions. Many of the resulting salts are more or less insoluble in water. Upon the insolubility of the carbonate, phosphate, and oxalate are based tests for calcium-ion in qualitative analysis (see p.

716). The presence of the element is most easily recognized by the brick-red color its compounds confer on the Bunsen flame, and by two bands — a red and a green one — which are shown by the spectroscope.

STRONTIUM Sr

The compounds of strontium resemble closely those of calcium, both in physical properties and in chemical behavior.

Occurrence. — The carbonate of strontium $SrCO_3$ is found as **strontianite** (Strontian, a village in Argyleshire). The sulphate, **celestite** $SrSO_4$, is more plentiful. The metal may be isolated by electrolysis of the molten chloride.

Compounds of Strontium. — The common salts (chloride, nitrate, etc.) are all made from the natural carbonate or sulphate. The former may be dissolved directly in acids, and the latter is first reduced by means of carbon to the sulphide, and then treated with acids.

Strontium-ion Sr^{++} is bivalent, and gives insoluble compounds with carbonate-ion, sulphate-ion, and oxalate-ion. The presence of strontium is recognized by the carmine-red color which its compounds give to the Bunsen flame (see also p. 509). Its spectrum shows several red bands and a very characteristic blue line. Salts of strontium, such as the nitrate, are used in the manufacture of red lights for fireworks and signals.

BARIUM Ba

The physical and chemical properties of the compounds of barium also recall those of calcium.

Occurrence. — Like strontium, barium is found in the form of the carbonate, **witherite** $BaCO_3$, and the sulphate $BaSO_4$, **heavy spar** or **barite** (Greek, βαρύς, heavy). The free metal, which is silver-white, may be obtained by electrolysis of the molten chloride.

The compounds are made by treating the natural carbonate

with acids directly, or by first reducing the sulphate with carbon to sulphide, or converting the carbonate into oxide, and then treating the products with acids.

Compounds of Barium. — Natural **barium sulphate** $BaSO_4$ is the source of many of the compounds. The precipitated sulphate, made by adding sulphuric acid to the aqueous extract from barium sulphide, is used in making white paint ("blanc fixe"), in filling paper for glazed cards, and sometimes as an adulterant of white lead. A mixture of barium sulphate and zinc sulphide ZnS, prepared in a special way, is called **lithopone:**

$$BaS + ZnSO_4 \rightarrow BaSO_4 \downarrow + ZnS \downarrow.$$
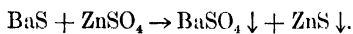
Made into paint it has greater covering power than white lead, does not darken with hydrogen sulphide as does the latter, and is non-poisonous. Barium sulphate is highly insoluble in water and is hardly at all affected by aqueous solutions of any chemical agents.

Barium monoxide BaO is manufactured from the carbonate. This, however, demands a much higher temperature than does calcium carbonate for its decomposition, the equilibrium tension of carbon dioxide not reaching one atmosphere until above 1350°. Special means must therefore be employed to assist the reaction. Heating with powdered charcoal is very efficient:

$$BaCO_3 + C \rightarrow BaO + 2CO.$$
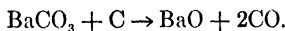
The oxide unites vigorously with water to form the hydroxide.

The monoxide, when heated in a stream of air or oxygen, gives **barium peroxide:** $2BaO + O_2 \rightleftarrows 2BaO_2$, as a compact gray mass. This change and its reversal constitute the basis of **Brin's process** for obtaining oxygen from the air. At a suitable high temperature, the air is forced in under pressure, causing the action to go forward, while the nitrogen escapes by a valve at the far end of the apparatus. Then, without change of temperature, by reversing the pumps, oxygen is taken out, and the reaction goes backwards. This alternation makes the process a continuous one. Barium peroxide is used in the manufacture of hydrogen peroxide.

Barium hydroxide $Ba(OH)_2$ is known in solution as "baryta-water." It is also the most stable of the three hydroxides, and may be melted without decomposition.

Barium-ion Ba^{++} is a colorless, bivalent ion. Many of its compounds are insoluble in water, and the sulphate is insoluble in acids also. The spectrum given by the salts contains a number of green and orange lines. The Bunsen flame is colored green. Salts of barium are employed, therefore, to give a green light in fireworks and night signals.

* Distinction between Calcium, Strontium and Barium Compounds. — The flame tests, described above, offer the quickest method of recognition.

In solutions of salts of calcium, strontium, and barium, the ions may be distinguished by the fact that calcium sulphate solution will precipitate the strontium and barium as sulphates, but will leave salts of calcium in dilute solution unaffected. Similarly, strontium sulphate solution precipitates barium sulphate, and does not give any result with salts of the first two.

Exercises. —* 1. Arrange the chromates of the metals of this family in the order of solubility (see Table). Compare the solubilities with those of the carbonates, oxalates, and sulphates.

2. Why do lime-water and baryta-water become milky when kept in an open bottle?

3. What will be the ratio by volume, at 150°, of the nitrogen tetroxide and oxygen given off by the decomposition of calcium nitrate? What would be the nature of the difference between the ratio at 150° and that at room temperature (see p. 392)?

4. How would you prove bleaching powder $CaCl(OCl)$ to be a *mixed salt* (p. 247), and not an equimolecular mixture of calcium chloride $CaCl_2$ and calcium hypochlorite $Ca(OCl)_2$?

5. Why does whitewash become so firmly attached to the wall?

6. What is the percentage of nitrogen in nitro-lime, assuming 100 per cent efficiency of conversion?

7. Make equations for the action of sodium palmitate: (a) upon calcium bicarbonate; (b) upon magnesium sulphate.

8. In softening water: (a) what would be the objection to using an excess of slaked lime; (b) why is prolonged stirring

required (p. 503); (c) why must the precipitate be removed by filtration?

9. Explain why wood ashes are sometimes used to soften water, and how they act.

10. Why does fluorite lower the melting-point of a slag?

CHAPTER 'XXXVI'

PLANT LIFE. CELLULOSE, STARCH AND SUGAR

THE chemistry of the metals and their compounds, while of the highest importance, is liable to grow tedious to the student, in consequence of the necessary similarities in the methods of presentation of successive elements. In order to mitigate the monotony, therefore, we shall intersperse at appropriate intervals throughout the text a few additional chapters dealing mainly with the elementary chemistry of carbon compounds. **Plant life** and **plant products** will first be discussed.

Plants and animals are similar in composition. They contain much the same elements, and these are present in the form of similar compounds. They differ sharply, however, in the foods they use in constructing these compounds. Plants use simple, inorganic materials; animals absolutely require complex, organic substances as food. The main chemical processes, therefore, are very different in the two groups.

How the Plant Feeds. — The walls of the cells which form the frame-work of a plant are made of **cellulose** $(C_6H_{10}O_5)_y$. In the cells, especially in certain parts of the plant, granules of **starch** $(C_6H_{10}O_5)_x$ are found. These complex substances differ in properties, although they have the same composition. The plant juice (sap) contains **sugars,** such as cane-sugar or sucrose, $C_{12}H_{22}O_{11}$, in variable amounts, and also **esters** (*vegetable oils,* p. 545) and **alkaloids** (*vegetable bases,* p. 594) in much smaller quantities. The plant cells also contain still more complex substances, known as **proteins.** *Gluten,* the sticky portion of wheat flour (p. 5), is a typical protein. These proteins are the chief components of the protoplasm, a semi-liquid substance lining each active plant-cell, and the real seat of life of the plant. Now

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all these substances contain carbon, hydrogen, and oxygen, and plant food must furnish these elements, which constitute over 95 per cent, on the average, of all. plants. Hence, in addition to large quantities of water ascending from the soil through the roots and stem, and sufficient amounts of compounds of nitrogen, potassium, phosphorus, and other elements, all plants require an abundant supply of carbon in absorbable form. This carbon is practically all taken up by plants in the form of atmospheric carbon dioxide. It is admitted through minute openings (stomata), situated mainly in the surface of the leaves.   '

The Reactions Involved. — Comparison of the formulæ of carbon dioxide CO_2 and of any plant substance, like starch $(C_6H_{10}O_5)_x$, shows at once that the latter contains a far smaller proportion of oxygen, relatively to the amount of carbon, than does the former. Hence, during the digestion or assimilation of the carbon dioxide by the plant, this compound must be *reduced*. In point of fact, the chlorophyll (green coloring matter) and protoplasm in the leaves act upon the carbon dioxide, causing oxygen to be liberated:
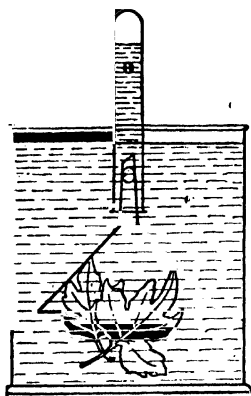
Fig. 114.

$$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2 \uparrow.$$
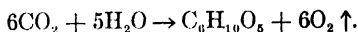
This action goes on only in the sun-light. The steps by which sugar, starch, and cellulose are manufactured by the plant out of water and carbon dioxide, are not yet perfectly understood. But the liberation of the oxygen is easily shown by placing a green plant under water in a jar, and setting the jar in the sunlight (Fig. 114). Bubbles of gas appear on the leaves, grow larger, and then detach themselves and rise to the top. The gas relights a glowing splinter of wood, and is pure oxygen.

The results of recent investigations suggest the following stages of the reaction:

(1) Carbonic acid, formed by the union of water and carbon

dioxide, is *reduced* to formaldehyde (p. 436), oxygen being liberated:

$$H_2CO_3 \rightarrow H.CHO + O_2.$$

(2) Formaldehyde molecules quickly combine together, or *polymerize*, to give simple sugars with the formula $C_6H_{12}O_6$:

$$6H.CHO \rightarrow C_6H_{12}O_6.$$
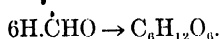
(3) These sugars lose a molecule of water, and *polymerize* further to form starch and cellulose:

$$nC_6H_{12}O_6 \rightarrow nH_2O + (C_6H_{10}O_5)_n$$
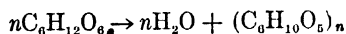
Reactions (1) and (2) have been carried out in the laboratory with ultra-violet light as a catalyst. Chlorophyll thus appears to act in the rôle of a *promoter* (compare p. 427), in the presence of which the reactions are able to proceed in visible light.

Reverse reactions also take place in the plant. Thus starch, which first accumulates in the leaves, is later turned back into a sugar soluble in the sap, and is thus able to pass to parts of the plant requiring new material. Some carbon dioxide is also liberated from plant surfaces by oxidation of sugars.

The Thermochemistry of the Reaction. — In the combination of carbon and oxygen, during combustion of wood or coal, much heat is liberated. Hence, when oxygen is taken out of carbon dioxide again, heat or energy in some form must be *supplied*. When this takes place in a plant, the energy is evidently furnished by the sunlight, for the action proceeds more slowly in the shade, and ceases in the dark.

The energy required can be measured, and may be expressed in calories. The energy required to produce one simple formula-weight of cellulose ($C_6H_{10}O_5 = 162$ g.) is 671,000 calories. The whole may be represented in a rough equation, in which the intermediate steps are left out, and only the starting substances and the final products are shown:

$$6CO_2 + 5H_2O + 671,000 \text{ cal.} \rightarrow C_6H_{10}O_5 + 6O_2.$$
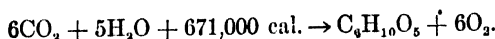
Cellulose $(C_6H_{10}O_5)_x$. — *This substance, named cellulose be-cause it forms the walls of the cells, composes much of the frame-work and intricate structure of plants.* We are familiar with pure cellulose in the forms of **filter paper** and **cotton**. The latter consists of fine, hollow tubes of cellulose (see A, Fig. 127, p. 591), large tufts of which surround the seed of the cotton plant. **Linen** is almost pure cellulose, **wood** is largely cellulose, and **paper pulp** is practically all cellulose.

Cellulose *interacts* with very few chemical substances. It is because it thus remains unchanged by most substances that come in contact with it, that it can be used as a filter paper. When it does undergo chemical change, it acts as if it contained hydroxyl (OH) groups, and behaves therefore chemically like an alcohol (see p. 595) forming valuable derivatives (explosives and plastics) which will be discussed later (Chapter XLII).

Paper Manufacture. — Paper is composed of cellulose $(C_6H_{10}O_5)_y$ and is made from a mixture of cotton or linen pulp and wood pulp — the cheapest varieties from the latter alone. The wood is cut into chips and heated ("cooked") with a solu-tion of calcium bisulphite $Ca(HSO_3)_2$. This dissolves out the lignin, which, together with cellulose, makes up the solid part of its structure. The pulpy material is then washed, beaten with water to reduce it to minute shreds, and bleached with very dilute chlorine-water. The pure cellulose, now paper pulp, suspended in water, is spread on screens, drained, pressed, and dried. During the process other substances are usually added. Thus size (glue or gelatine) prevents the ink from running; pulverized calcium sulphate (gypsum), and other white solids ("loading") give body to the paper and make possible the subsequent production of a smooth surface by rolling ("calendering"). Ultramarine (blue) and other colored powders are added to the pulp when special tints are required.

Other Uses of Cellulose. — Cellulose dissolves in hot, con-centrated zinc chloride solution. When the liquid is pressed through a small orifice into alcohol, the cellulose is reprecipitated in the form of a thread. By carbonizing, this is made into **fila-ments** for incandescent electric lamps.

Cellulose is soluble also in a solution of cupric hydroxide in excess of ammonium hydroxide, and is reprecipitated by dilute sulphuric acid. Paper or cotton goods can be passed through first one and then the other of these liquids, and so receive a tough, **waterproof surface**. **Artificial silk** is made by pressing the solution through dies into the precipitant. It can be dyed to any desired tint, and is at least as brilliant in appearance as the natural article. Its strength, however, does not equal that of the natural silk fibre, especially when wet.

Cotton, when dipped in strong sodium hydroxide solution, and then stretched while drying to prevent the shrinkage which otherwise occurs, acquires a brilliant luster and is used in enormous quantities under the name of **mercerized cotton**.

Finally, mercerized cotton, or wood pulp treated with caustic soda, combines with carbon disulphide to give **viscose**. Viscose dissolves in water, and decomposes in solution giving a plastic form of cellulose. This can be rolled into transparent sheets, made into caps for bottles, moulded into any form, or pressed through dies into solutions of salts of ammonium to give another form of artificial silk.

Starch $(C_6H_{10}O_5)_x$. — Starch is found in plants in little *colorless granules* of various rounded shapes (Fig. 115) which may readily be seen under the microscope. These granules are massed in large numbers in the ears of wheat and oats, in the tubers of potatoes, in the grains of maize (corn) and in peas and beans. Even in the leaves they can be seen, immediately after the plant has been exposed to sunlight.

Fig. 115.

They gradually disappear from the leaves in the dark. They can be recognized, not only by their appearance, but, without a microscope, by the **iodine test**. When a drop of a potassium iodide solution, rendered brown by the addition of a little free iodine, is placed on the leaf or other part of the plant, the granules of starch become *blue* (compare p. 5) while the other parts are **not affected**.

Preparation of Starch. — If flour, which is made by grinding wheat, and is three-fourths starch, is placed in a muslin bag and kneaded under water, the granules of starch are washed out and render the water milky (p. 5). After a time the granules settle and the water can be poured off. Starch is manufactured by washing disintegrated potatoes (in Europe) or maize (in America) on sieves, and collecting and drying the white powder deposited in the water used for the washing.

Starch is *not soluble* in water. If it is boiled with water, however, the granules swell and break, and the starch becomes finely diffused through the water, forming a clear liquid. With little water, a sort of transparent jelly is produced. When the liquid is poured through a filter, a large part of the starch goes through the paper as if it were truly dissolved. Such a state is called a **colloidal suspension** (p. 138). Imitation solutions like this are constantly met with in using complex organic compounds such as enter into jellies, glues, soaps, and the juices of the bodies of animals. Even inorganic substances, of the insoluble class, give such suspensions. A description of their peculiarities must be noticed under soap (pp. 553-554).

The colloidal suspension of starch is *used* in the laundry, for stiffening white goods. Glucose is manufactured from it.

Since neither cellulose nor starch can be vaporized without decomposition, and since they do not form true solutions in any of the common solvents, we have no means of determining their molecular weights, and are therefore forced to write their formulæ in the indeterminate forms $(C_6H_{10}O_5)_y$ and $(C_6H_{10}O_5)_x$ respectively. The molecule in each case is, in all probability, exceedingly complex.

Glucose $C_6H_{12}O_6$ from Starch. — When starch is boiled with water, to which a few drops of an acid (catalyst) such as hydrochloric acid have been added, the liquid, after neutralization of the acid, is found to be sweet in taste. A kind of sugar, **glucose** $C_6H_{12}O_6$, can be obtained in crystals by evaporation. In commerce the evaporation is stopped before crystallization begins, and the syrup ("corn-syrup," if maize is the source of the starch) is sold for making candy and for preserving fruits.

$$\bullet \ (C_6H_{10}O_5)x + xH_2O \rightarrow xC_6H_{12}O_6.$$
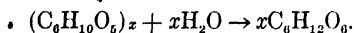
Glucose is known also as **dextrose** and as **grape sugar**. Brownish crystalline granules found in dried grapes (raisins) are mainly composed of it. When pure, it is almost colorless. It *reduces* cupric hydroxide, in Fehling's solution (p. 609), to cuprous oxide.

The Sugars. — The common sugars are divided into two classes. There are several sugars, having the same formula, $C_6H_{12}O_6$, but different properties, which are called **monosaccharides**. Other sugars, having twice as many carbon units in the formula $C_{12}H_{22}O_{11}$, are called **disaccharides**. The sugars we have occasion to mention here are the following:

Monosaccharides: Glucose (dextrose or grape sugar) $C_6H_{12}O_6$.
    •   Fructose (fruit sugar) $C_6H_{12}O_6$.
Disaccharides: Sucrose (cane-sugar, beet-sugar, saccharose) $C_{12}H_{22}O_{11}$.
    Maltose (formed by action of malt on starch) $C_{12}H_{22}O_{11}$.
    Lactose (milk-sugar, found only in animals) $C_{12}H_{22}O_{11}$.

Carbohydrates. — Since cellulose, starch and the sugars are freely changed, one into another, they are grouped together in one class, the **carbohydrates**. The word refers to the fact that they contain hydrogen and oxygen in the proportions required to form water, and are, therefore, in a sense, hydrates of carbon. When dehydrating agents like concentrated sulphuric acid (p. 345) act on the carbohydrates, a black mass of carbon is left.

Sucrose or Cane-Sugar $C_{12}H_{22}O_{11}$. — The sugar-cane and the beet produce exceptionally large amounts of this sugar, which is the one commonly used as table sugar. Maple sugar, obtained by evaporating the sap of the tree, is composed mainly of the same substance.

The sugar-cane forms stalks from ten to twelve feet high. The juices are extracted by crushing the plants between rollers. The liquid is evaporated in closed pans. A vacuum maintained

in the pans permits the boiling of the solution at a low temperature (about 65 degrees) and prevents the decomposition of a part of the sugar which would otherwise occur. When the syrup cools, the sugar crystallizes and the crystals are freed from the liquid in centrifugal machines. The crystals are brown in color. At the sugar refinery they are dissolved, and the solution is passed through a column of bone charcoal. This adsorbs the coloring matter, and the filtrate is once more evaporated and allowed to crystallize. Refined cane-sugar has a faint yellow tint, and a small amount of ultramarine is added to cover up this tint, and give the white appearance which is popularly connected with purity in sugar.

The sugar beets, which contain 16 per cent or more of cane-sugar, are sliced and steeped in water to extract the sugar. The liquid contains gummy material in colloidal suspension. This is coagulated and precipitated by adding "milk of lime" (calcium hydroxide $Ca(OH)_2$ suspended in water) and boiling. Carbon dioxide is then passed through the solution to precipitate the excess of lime:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O.$$
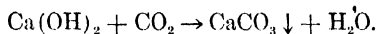
The solution is decolorized with charcoal and evaporated to crystallization in the same way as is the extract from the sugar-cane.

Properties of Sucrose. — Sucrose *crystallizes* in four-sided prisms, the form of which is seen in "rock-candy." It *melts* at 160°. It does not reduce Fehling's solution (p. 517). When heated to 200 to 210° it begins to decompose, slowly losing water and leaving a brown, soluble mass called **caramel**, used in coloring whisky and soups.

When boiled with water, to which a trace of an acid catalyst has been added, it is *hydrolyzed*, giving a mixture of the two monosaccharides, glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$
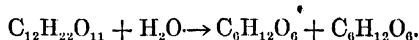
This mixture of glucose and fructose is called **invert sugar** and is found in many sweet fruits and in honey. Each sugar

interferes with the crystallization of the other, by lowering the freezing-point (p. 218), and so invert sugar is added in making "fondant" candy and candy that is to be "pulled," both of which are intended to remain soft for some time. With the same object in view, vinegar, lemon juice, or cream of tartar is added to a syrup made from cane-sugar, in order that the acid contained in them may produce some invert sugar and so give a less crystallizable mixture (icing for cakes). Prolonged heating has the same effect.

Exercises. — 1. What inference do you draw as to the composition of tapioca, sago, and rice from the facts that they are plant products and when boiled with water and cooled give a jelly-like mass? How should you confirm your inference?

2. (a) Why does a concentrated solution of sugar boil at a temperature far above that of boiling water? (b) In evaporation why is the boiling-point lower in a vacuum than in air?

3. In what relative volumes are carbon dioxide used and oxygen produced by a plant?

4. What products must be formed when paper is burned? Make the equation.

CHAPTER XXXVII

PLANT GROWTH. OSMOSIS. FERTILIZERS

FOR successful growth, plants require carbon, hydrogen, oxygen, phosphorus, potassium, nitrogen, sulphur, calcium, iron, and magnesium. The carbon is chiefly supplied by the carbon dioxide in the air, as we saw in the preceding chapter. Water supplies hydrogen and oxygen, entering through the leaves, and also through the roots and stems. Oxygen is also supplied directly by the air. Phosphorus, nitrogen, and sulphur are absorbed from the soil by the roots as soluble phosphates, nitrates, and sulphates, and nitrogen sometimes as ammonia. Potassium commonly enters as carbonate or bicarbonate. Calcium and magnesium are absorbed as phosphate, nitrate, sulphate, or bicarbonate; and iron as ferric hydroxide ($Fe(OH)_3$). Manganese, chlorine and silicon are also present in many plants. In some species, sodium salts can take the place of potassium salts.

• The last-named elements are used in such small amounts relative to the available supply in the soil, that they rarely need attention. **Nitrogen, phosphorus, potassium** and **calcium,** however, the presence of which in quantity is essential to the life and development of plants, often need to be added to soils which are deficient in these elements. Suitable compounds are therefore used in enormous quantities as fertilizers.

Before discussing individual fertilizers, we may profitably take up the general question of how the plant derives its food from the soil.

How the Plant Feeds. — We have mentioned (p. 511) that the plant juice or sap contains soluble sugars, which travel to

those parts of the plant which require new material for their growth. The moist walls of the root-hairs of the plant are freely permeable to *water*, the entrance of which into the plant from the soil is necessary to offset evaporation from the leaves and stems. Soluble salts present in the soil water are also able to pass, although less freely, through these walls, and are incorporated in the sap. If they are of nutritive value to the plant, they react, as they circulate through the plant from cell to cell, with the organic constituents there present, forming more complex compounds which are unable to permeate the boundary walls of the cells, and thus become permanently fixed in the growing parts. If they are not of nutritive value, they complete the circuit unchanged.

Now the passage of salts from the soil water into the plant continues only until the sap inside contains the same concentration of each salt as the solution outside. Hence while *nutritive* constituents, which are removed from the sap during its circulation through the plant, can continuously enter to keep up the supply necessary for growth, *non-nutritive* constituents soon reach their equilibrium concentration and are thereafter rejected.

Osmosis. — The membranes lining the cell walls and the root-hairs of plants exercise, as we saw above, a *selective action* with regard to the passage of different substances through them Water is able to permeate the membranes quite freely, dissolv salts pass through less readily, while the movement of compl organic substances, such as proteins, is completely blocked. Up this selective flow of materials through the plant membranes, must be noted, the life of a plant is absolutely dependent. If t membranes were freely permeable to the organic materials co tained in the plant sap, the plant would soon lose these materi to the outside soil and die of exhaustion.

The selective flow of certain components of a solution throu a membrane is known as **osmosis.** Osmosis and its consequence, **osmotic pressure,** are phenomena which may be very clearly illustrated in the laboratory by means of a solution of cane sugar and an artificial membrane of precipitated cupric ferrocyanide $Cu_2.Fe(CN)_6$.

· **Osmotic Pressure.** — A suitable *semi-permeable membrane* may be obtained by soaking a clean porous pot in a solution of potassium ferrocyanide $K_4.Fe(CN)_6$ (p. 704), rinsing in water, and then allowing to stand in a solution of cupric sulphate. The diffusion of the latter substance into the cell produces, by double decomposition, a film of insoluble copper ferrocyanide within its walls. This film is freely permeable to water molecules, but not to molecules of sugar dissolved in the water.

A simpler method is to use a *diffusion shell* of specially treated parchment, of test-tube form. This, however, is not entirely impermeable to sugar molecules.

The porous pot or diffusion shell, filled with sugar solution, is securely attached to a long glass tube, and suspended in pure water (Fig. 116). It is found that the level of the liquid in the tube gradually rises until, if the membrane remains intact and is truly impermeable to sugar, a definite hydrostatic pressure is established, the magnitude of this *osmotic pressure* depending only upon the temperature and upon the fraction of sugar molecules in the solution within the cell.
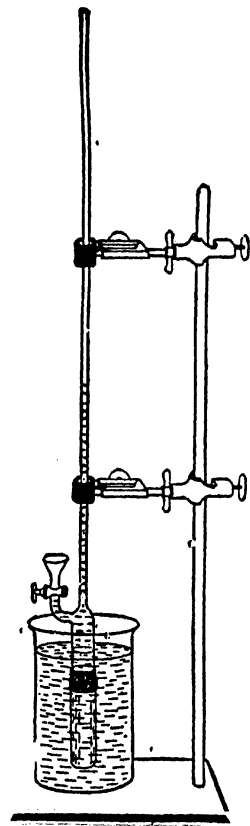
Explanation of Osmotic Pressure. — For a complete discussion of osmotic pressure, the reader is referred to a *modern* text-book of physical chemistry. A brief explanation by means of the molecular hypothesis, however, may be given here.

Fig. 116.

The molecules of water in the pure water outside the cell, and the molecules of water and of sugar in the solution inside the cell, are all in rapid motion (p. 144). When, in consequence of this motion, they strike the membrane, water molecules have a chance of passing through, but sugar molecules are all turned back. Now the concentration of water molecules in the pure water *outside*, striking the membrane and attempting to enter the cell, is *greater* than the concentration of water molecules in the solution *inside*, striking the membrane and attempting to leave the cell (compare vapor pressures, p. 153). Hence more water molecules will be entering than leaving, and the level of the liquid inside the tube must rise in consequence.

Why does the level of the liquid stop rising when a definite hydrostatic head has been established? Because now, although there is still a greater concentration of water molecules in the pure water outside than in the solution inside, water molecules attempting to enter the cell through the membrane are *opposed* by the hydrostatic pressure, while water molecules attempting to leave are *assisted* in their passage. We have on one side of the membrane *more* water molecules with a *smaller* chance of getting through, on the other side *fewer* water molecules with a *greater* chance of getting through. Equilibrium is reached, evidently, when these two factors counterbalance.

The student should note very carefully the fact that *the sugar molecules are not directly concerned in the phenomenon of osmotic pressure.* Their function is merely to *reduce the concentration of water molecules* in the solution inside the cell. Any solute, with respect to which the membrane is similarly impermeable, will give the same effect, the osmotic pressure at any given temperature being dependent only upon *the fraction of solute molecules in the solution*, that is, upon the extent to which the concentration of *water* molecules has been reduced (compare, again, vapor pressure depression of solutions, p. 153).

A solution containing 1 g. molecular weight of an inert solute dissolved in 1000 g. water should give at 20°, with a perfectly semi-permeable membrane, an osmotic pressure of 23.6 atmospheres.

Osmotic Pressure and the Gas Laws. — It may be shown, by the use of thermodynamics, that the osmotic pressure of an exceedingly dilute solution is, under certain assumptions, practically identical with the gaseous pressure which the solute would exercise if the solvent were suddenly annihilated and the solute were to exist, in the space formerly occupied by the solution, in the state of a gas. This fact, first demonstrated by Van't Hoff in 1885, has led many chemists to consider osmotic pressure an exact analogy of gaseous pressure and to assume that the gas laws are fundamentally applicable to dilute solutions. Such a point of view proved, indeed, of extreme value in the early theoretical development of the properties of solutions. Unfortunately, however, the tendency to press the analogy too far was seldom resisted.

It cannot be too strongly emphasized that osmotic pressure bears no direct relation at all to gaseous pressure, and the true osmotic pressure equation is quite distinct from any possible gas equation. The laws for a *perfect gas* are represented by the statement: $PV = RT$ (where P is the pressure, V the volume occupied by one gram-molecular weight of the gas, T the absolute temperature, and R a constant). The osmotic pressure equation for an *ideal solution,* omitting a small correction for compressibility, may be written: $\Pi V = RT \log_e x$ (where Π is the osmotic pressure, V the volume occupied by one gram-molecular weight of the *solvent,* and x the molecular fraction of the *solvent* in the solution). This admittedly reduces to the perfect gas equation when the solution is infinitely dilute, but the student with any knowledge of mathematics will recognize that two functions may possess the same limiting value without being related in any way. As has been shown in the preceding section, it is the solvent, not the solute, that is directly concerned in the phenomenon of osmotic pressure, and any attempt to correlate the properties of solutions of finite concentration with the gas laws, neglecting the solvent entirely, is certain to lead to confusion.

According to the modern view-point, any solute in a liquid solution must be assumed to exist, however great its dilution, not in the gaseous but in the **liquid** state (see p. 144).

Osmotic Pressure in Plant Life. — Osmotic pressure was first studied by Pfeffer, a botanist, in 1877. De Vries (1878) used plant cells for the same purpose. The cells included a liquid containing various salts in solution, and a protoplasmic layer which lined, but was not firmly attached to, the cell wall. This protoplasmic layer behaved like an imperfect semi-permeable membrane. When such cells were immersed in a concentrated solution of any substance, the water passed from the interior of the cell to the solution, and by means of a microscope a shrinkage of the protoplasmic layer away from the cell wall could be observed. Conversely, when such cells were placed in pure, water, or a solution of a very dilute nature, water passed from the outside into the interior, and the protoplasmic layer was distended so as to cause the cell to become turgid.

Osmotic pressure is, therefore, a subject of great interest in connection with the physiology of plants. It aids in explaining why a withered flower, containing a solution in its cells, revives when placed in pure water. The latter enters through the walls of the cells, and the pressure thus produced distends the structure and stiffens it. Similarly, the wilting of plants, when too high a concentration of salts as fertilizers is added to the soil, is explained. In the animal body also, osmosis plays a large part.

Fertilizers. — Many soils are either naturally deficient in one or more of the necessary plant foods, or the supply may have been exhausted by repeated cropping. Every crop removes permanently a certain part of the supply. Thus, in the case of nitrogen, an average crop of maize or corn (45 bushels) removes 63 pounds per acre, a crop of cabbage (15 tons) removes 100 pounds per acre, clover hay (2 tons) 82 pounds, and wheat (15 bushels) 31 pounds. When the supply becomes reduced, the crops become poor. Moreover, the necessary elements must be present in *soluble form,* or they cannot enter into the plant system.

Felspar $KAlSi_3O_8$ is a common constituent of, many rocks, such as granite (p. 4). When such rock material, contained in the soil, is decomposed by *weathering,* through the action of car-

bonic acid from the atmosphere, the felspar gives *clay* $HAlSiO_4$ and soluble compounds of potassium. There are immense quantities of felspar available, but the process of weathering is very slow, and in many agricultural regions the soil is therefore deficient in soluble salts of potassium.

It is just as necessary to feed crops as to feed cattle, and equally foolish to starve either of them. Fertilizers are used to make good the original, or acquired deficiences of the soil in the most important elements, *nitrogen, phosphorus, potassium* and *calcium*. It is absolutely necessary, in addition, to keep up a sufficient supply of fresh organic material in the soil, or the use of fertilizers may result in more harm than benefit.

The value of the systematic use of fertilizers is indicated by comparison of the average crop of wheat per acre in different countries. The average of ten successive years is: Denmark 40 bushels, Great Britain 33, Germany 29, United States 14.

Nitrogen. — The nitrogen is supplied as sodium nitrate or guano (p. 489), calcium nitrate (p. 394), ammonium sulphate (p. 485), calcium cyanamide (p. 505), manure or the offal ("tankage") and ground bones from slaughter houses.

Over every acre of the earth's surface there are 34,000 tons of **free atmospheric nitrogen.** Plants in general are incapable of drawing upon this immense store for the nitrogen necessary for their growth, but peas, beans, clover, alfalfa and other leguminous plants bear round their roots colonies of a special kind of bacteria which has the power to bring free nitrogen into combination. In these **root nodules** (Fig. 117) the bacteria first produce proteins, which later decompose, and ultimately yield nitric acid. In this way a crop of clover will fertilize the soil, not only for itself, but also for the following crop. The advantage of rotation of crops is therefore explained.

Fig. 117.

The beneficial action of bacteria upon plant growth is not limited to this special case. The soil is crowded with bacteria

which assist in the decomposition or rotting of vegetable and animal matter. The product, the black, gummy stuff of a fertile soil, is called *humus*. Certain varieties of bacteria convert insoluble carbohydrates such as cellulose into simpler soluble materials, immediately available for plant use. Other species liberate the nitrogen from proteins in the form of *ammonia* and *amino-compounds* (p. 441). Others, again, oxidize these compounds to *nitrous acid* and *nitrites*. Still others, finally, oxidize these products to *nitric acid* and *nitrates*.

' The actual assimilation of nitrogen by plants, in whatever form that element is originally present in or added to the soil, takes place almost exclusively through soluble nitrates. The co-ordinated team-work of all of the above classes of bacteria is therefore an essential point in the efficient utilization of other nitrogen-containing fertilizers.

Phosphorus. — Natural calcium phosphate $Ca_3(PO_4)_2$ is the orthophosphate of calcium. It is found in considerable deposits in S. Carolina, Florida, Tennessee, and several western states, and in Algeria and Tunis. This insoluble salt, however, affords only an exceedingly dilute phosphorus diet for plants. Hence, a more soluble compound is to be preferred. This is found in *calcium acid-phosphate* ("superphosphate") $CaH_4(PO_4)_2$, which is made by heating pulverized natural calcium phosphate with sulphuric acid containing the requisite proportion of water:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \rightarrow CaH_4(PO_4)_2 + 2(CaSO_4,2H_2O).$$
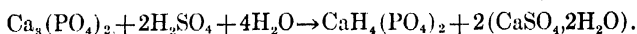
The whole turns into a dry mixture, consisting of the superphosphate and gypsum (hydrated calcium sulphate). The latter does not interfere with the fertilizing power of the soluble superphosphate, so the mixture is placed directly in sacks and sold as "superphosphate of lime."

In slaughter houses the bones, after being deprived of fat and gelatin, give a residue which is rich in *calcium phosphate*. This residue is treated with sulphuric acid and made into fertilizer.

Potassium. — *Wood ashes* contain much potassium carbonate, and are used as fertilizers for this reason. The giant seaweeds (*kelp*) of the Pacific coast have also been found to contain an

unusually large proportion of salts of potassium. By far the most important source of this element, however, is *potassium chloride*, obtained from natural salt deposits.

The average production of the German deposits at Stassfurt in the ten years preceding the war exceeded 1,000,000 tons (calculated as K_2O). These deposits constituted practically a world monopoly, and the shortage of potassium salts for fertilizer purposes during the war was consequently extreme. The most strenuous efforts to develop the potassium resources of the United States (natural brines, kelp, recoverable by-products from the cement and molasses industries, etc.) culminated in a production of only 50,000 tons K_2O in 1918. Fortunately, the cession of Alsace to France has destroyed the German monopoly, since very extensive deposits exist near Mulhouse. The working of these deposits has been greatly hampered by the damage done to shafts and machinery by the Germans before their evacuation, but production in 1920 already exceeded 200,000 tons K_2O.

Potassium chloride occurs in the Stassfurt deposits as *sylvite* KCl, but is chiefly associated with magnesium chloride as *carnallite* $KCl,MgCl_2,6H_2O$. When water is added to carnallite, a large part of the potassium chloride, which is much less soluble, separates out. Complete extraction and purification of the salt involve a series of recrystallizations. The Alsace deposits contain very little magnesium salts, and the separation of the potassium chloride from the sodium chloride with which it is mixed is comparatively simple.

Potassium sulphate is also obtained from salt deposits, and is substituted for potassium chloride as a fertilizer for certain crops, such as tobacco. Chlorides, in general, melt at lower temperatures than sulphates, and the presence of a chloride in tobacco results in an ash that fuses on burning. This is, obviously, an undesirable property, especially for cigars.

Calcium. — Calcium is naturally present in many soils as *calcium carbonate* $CaCO_3$. In contact with water containing carbonic acid (see p. 501), this gives a solution of the more soluble *bicarbonate* $Ca(HCO_3)_2$. Other compounds of calcium which are used as fertilizers include lime CaO or $Ca(OH)_2$, calcium phos-

phate and acid phosphate, calcium sulphate or gypsum (p. 500), and calcium cyanamide.

Manure. — One ton of farm manure contains about 10 pounds of nitrogen (chiefly as urea $CO(NH_2)_2$ and proteins), 5 pounds of phosphoric acid and 10 pounds of potash. The manure is mixed with the soil just before planting seed, or is used as top dressing.

The bacteria in the air and in the soil assist materially in the changes in the manure. Thus urea is hydrolyzed to ammonium carbonate $(NH_4)_2CO_3$:

$$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3.$$
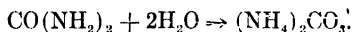
The proteins are changed by air bacteria into ammonia. The formation of nitrates seldom happens in manure piles, but scattered manure, with the help of soil bacteria, develops nitrates.

The potassium compounds form potassium hydrogen carbonate $KHCO_3$. The phosphorus and sulphur compounds become soluble phosphates and sulphates.

Indirect Fertilizers. — Not all substances which are added to the soil are employed with the direct object of their assimilation for plant growth. Often indirect effects induced by their presence are of greater importance. A few cases where calcium salts are of service as indirect fertilizers may be briefly presented as illustrations of this point.

(1) *Gypsum* $CaSO_4,2H_2O$ is added to manure at the rate of 100 pounds per ton. This slightly soluble salt reacts in the soil solution with the ammonium carbonate produced by the hydrolysis of urea, precipitating the much less soluble calcium carbonate and leaving ammonium sulphate in solution:

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3 \downarrow.$$
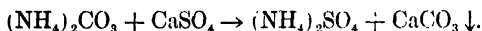
Now ammonium sulphate, being a salt of a *strong* acid with a *weak* base, is only very slightly hydrolyzed in solution (see p. 326). Ammonium carbonate, however, is a salt of a *weak* acid and a *weak* base, and is extensively hydrolyzed. This hydrolysis, unless a large excess of water is present, would lead to rapid loss of ammonia from the manure. The smell of free ammonia, in-

deed, is often very noticeable in manure piles. The addition of gypsum *fixes* this valuable constituent in the fertilizer for plant use. Lime, on the other hand, would assist in the *liberation* of ammonia.

(2) Gypsum is often added, also, to clay soils with the object of converting insoluble compounds of *potassium* into more soluble compounds. Lime and calcium carbonate are employed to change 'insoluble *phosphates* of iron and aluminium into more soluble calcium phosphates.

(3) Some soils are either naturally acidic or *sour*, or have become so by excessive use of sulphate fertilizers, and are hence unfavorable to plant growth. This acidity is corrected by addition of lime or calcium carbonate, but *not* gypsum.

(4) Salts which are *injurious* to plants, such as soluble magnesium compounds or "black alkali" (sodium carbonate), are converted into less soluble compounds, such as magnesium hydroxide or carbonate, by addition of lime or calcium carbonate, or into non-poisonous compounds, such as sodium sulphate, by gypsum.

Adsorption in Soils. — As we have seen, fertilizers *must* contain the elements necessary for plant growth in soluble form. It is undesirable, however, to use salts which are exceedingly soluble in water as fertilizers, since they will obviously be rapidly washed away from the surface soil. A large proportion of all fertilizers is unavoidably wasted in this manner. The minute particles of the soil, however, possess the power of conserving dissolved substances in the soil solution by concentrating and holding them upon their moist surfaces. This phenomenon, *adsorption,* is of considerable interest and importance in other connections, and will be taken up in detail in later chapters (pp. 536, 556, 590).

Exercises. — 1. Given an osmotic pressure cell and an unknown substance, soluble in water, to which the membrane is perfectly impermeable, how could you determine the molecular weight of the substance?

2. What would be the effect of putting fresh flowers in a vase containing a concentrated salt solution?

3. At 20° 100 c.c. of water, shaken up with excess NaCl and KCl, dissolve 30 g. NaCl and 15 g. KCl. At 100° the same amount of water, in equilibrium with the same two solids, contains 20 g. NaCl and 40 g. KCl. On the basis of these figures, devise a method for separating KCl from NaCl in the Alsace deposits.

4. The use of ammonium sulphate as a fertilizer is apt to result in an *acid soil*. Explain why.

5. What are the three elements most needed in fertilizers? Of which does every country have a free and unlimited supply? How can it be made available?

6. What valuable soil ingredients are lost to a locality when a carload of wheat is shipped away? A carload of pure sugar? Of cotton, (*a*) ginned or (*b*) unginned? Of cotton-seed oil (p. 546)?

CHAPTER XXXVIII

PLANT PRODUCTS. FERMENTATION AND FUELS

HAVING described the chemistry of plant life and growth, we may now proceed to the chemistry of substances resulting there-from. Foods will be taken up separately in the following chapter. In the present chapter we shall restrict ourselves to two other main branches, **fermentation products** and **fuels.**

Enzymes. — All fermentations are brought about either directly or indirectly by the activities of animal or vegetable organisms. The most familiar ferment, of course, is **yeast.**

Yeast belongs to a low order of plants and consists of minute cells. Its value lies in the fact that, while growing and multiplying, it secretes within each cell small amounts of two very active chemical substances which are dissolved in the cell contents. These substances are known as **zymase** and **invertase** (or **sucrase**), and belong to the class of organic materials called **enzymes.** Enzymes produce remarkable chemical changes in organic materials by their mere presence (contact actions). These changes are *specific*, each enzyme acting only on certain carbohydrates, for example, and being quite inert towards others.

Fermentation of Sugars. — When a cake of yeast is broken into an aqueous solution of glucose or grape-sugar (p. 516), the small amount of zymase present causes the gradual decomposition of the sugar. The most favorable temperature is about 30°. Bubbles of carbon dioxide soon begin to rise to the surface, and the gas can be led off (Fig. 118) to exhibit its characteristic action (p. 424) on limewater. At the same time **alcohol** C_2H_5OH accumulates in the liquid as the sugar disappears:

$$C_6H_{12}O_6 \rightarrow 2CO_2 \uparrow + 2C_2H_5OH.$$

532
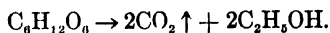
The liquid extracted from the yeast cells works as well as does the plant itself.

Yeast will ferment fructose (fruit sugar, p. 517), with the same result, but more slowly.

Zymase does' not act upon cane-sugar (sucrose $C_{12}H_{22}O_{11}$). But the invertase (sucrase), which is also contained in the yeast, hydrolyzes the sucrose in the same way as does a dilute acid, giving invert sugar (p. 518). The latter is then decomposed by the zymase. Hence cane-sugar in solution is decomposed by yeast into alcohol and carbon dioxide, just as is grape-sugar, only more slowly.

In the manufacture of **wines** the glucose contained in the grape juice is fermented by a species of yeast always found on the skins.
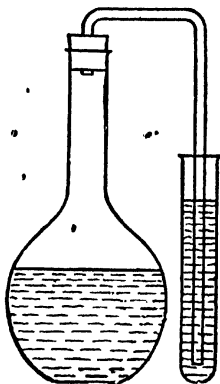
Fig. 118.

Fermentation of Starch. — Barley, which has been allowed to sprout, and is then dried, is called **malt.** This contains an enzyme, **diastase** (or **amylase**), which is able to hydrolyze starch into maltose $C_{12}H_{22}O_{11}$ (p. 517). Maltose is further hydrolyzed by another enzyme, **maltase,** to form glucose, and the latter is then decomposed by zymase into alcohol and carbon dioxide.

Whisky is made by treating the starch of rye, maize, or barley in the above way, with subsequent distillation. **Beer** is made similarly from various kinds of grain, particularly barley, except that the fermented liquid is not distilled.

Industrial Alcohol. — Alcohol has very extensive uses, apart from its historic value as a beverage. It is employed as a *solvent* in making varnishes for wood and lacquers for metal, as well as for plastics like celluloid, collodion and artificial silk (p. 515). It is of service in the *purification* of many natural organic products, such as *turpentine,* and in the *preparation* of many synthetic organic products, such as *dyes.* It is also rapidly coming

into use as a *fuel*, its smokeless flame and efficiency of combustion making it of special importance for aeroplane and motor engines. *Solidified alcohol*, obtained by the addition of cellulose esters (p. 595), is now largely employed for *cooking* purposes. Another new development is the catalytic production of ethylene for *cutting and welding* purposes (p. 440).

Alcohol, as used in the industries, is *denatured*, or rendered unsuitable for drinking purposes, by addition of small quantities of benzine (p. 433), pyridine bases, or other disagreeable and non-removable organic liquids. The exact formula of denatured alcohol depends upon the use for which it is intended.

The cheap production of industrial alcohol is rendered possible by the utilization of certain waste materials rich in carbohydrates. When the price of food is high, *grains* are employed in the manufacture of alcohol only when a crop has been damaged in some manner so that it cannot be sold as a food material. When *sawdust* or *wood refuse* is heated with dilute sulphuric acid under pressure, the cellulose is converted into fermentable sugars by hydrolysis (compare p. 516). At the present time, however, the most important source of industrial alcohol in the United States is *molasses*. Only a few years ago the disposal of molasses furnished a very troublesome problem to the sugar mills, but in 1918 nearly 120,000,000 gallons of industrial alcohol were obtained from this "waste product" in the United States alone.

Acetic Acid CH₃COOH. — This acid is formed by the partial oxidation of alcohol (p. 437). **Vinegar** (crude acetic acid) is manufactured by oxidizing alcohol with atmospheric oxygen, using a bacterium (*B. aceti*, "mother of vinegar"), or more probably an enzyme which it secretes, as a contact agent. The dilute alcohol, in the form, for example, of "hard" cider (fermented apple juice), is allowed to trickle over shavings in a barrel. The shavings are inoculated with the *B. aceti* by preliminary wetting with vinegar. Holes in the sides admit a plentiful supply of air, to the action of the oxygen of which the liquid is exposed by being spread over the surface of the shavings:

$$C_2H_5OH + O_2 \rightarrow CH_3.COOH + H_2O.$$
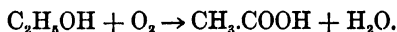
The liquid (vinegar), which issues at the bottom, contains from 5 to 15 per cent of acetic acid, besides coloring and flavoring matters derived from the fruit juices.

Pure acetic acid may be prepared by distilling the vinegar repeatedly. It is derived more cheaply, however, from the liquid distillate obtained by heating wood in the manufacture of charcoal. Large quantities are used in the manufacture of various synthetic organic products (see, for example, p. 595).

FUELS

Destructive Distillation of Wood. — When dry wood is heated in iron retorts in absence of air, the compounds which it contains are decomposed. Much of the carbon remains in the form of **charcoal.** The vapors which pass off (through the pipe on the right, Fig. 119) deposit, when cooled, much **liquid material.** The uncon-
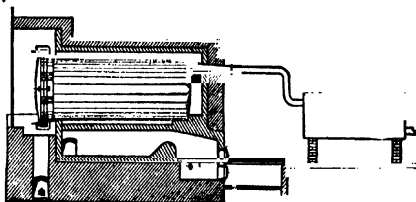
Fig. 119.

densed **gases** are combustible and are used for heating the retorts or other similar purposes. Hard wood furnishes, approximately, 25 per cent of its weight of charcoal, 25 per cent of gases, and 50 per cent of liquids. The liquid contains acetic acid (10 per cent), methyl alcohol CH_3OH or wood spirit (3 per cent), a complex tarry mixture used in road-making (10 per cent), water (77 per cent), and a little acetone (p. 437). The distillate from resinous wood also contains valuable quantities of *turpentine*, $C_{10}H_{16}$, an unsaturated hydrocarbon used extensively as a solvent. The gases evolved contain a large part of the nitrogen of the original proteins in the form of ammonia, which is dissolved out with water.

When charcoal only is desired, the wood is stacked, covered with turf (Fig. 120), and set on fire. A part is burned, the rest is converted into charcoal, and all the valuable volatile products are lost.

. **Properties of Wood Charcoal. Adsorption.** — The charcoal retains the structure — a complex network of minute cells — of
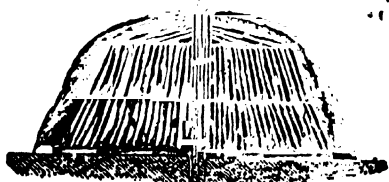
the original wood, and therefore has a *surface* which is vast in proportion to the amount of material it contains. Upon this surface it is capable of taking up or adsorbing many times

Fig. 120.

its own volume of gases, especially of the more condensible ones. Thus, boxwood charcoal takes up ammonia (90 volumes), hydrogen sulphide (55 volumes), and oxygen (9 volumes).

The adsorption is extremely rapid and, in the case of a condensible gas contained in small quantity in air, practically complete. For this reason, charcoal and other substances with very finely divided surfaces are used as adsorbent materials for industrial gases and vapors (compare silica gel, p. 452).

The **toxic gases** employed in the Great War are also readily adsorbed by charcoal. Hence the canisters of gas masks contain layers of porous charcoal, together with granulated soda-lime and potassium permanganate, which react *chemically* with certain of the noxious gases liable to be present. During the war vast strides were made in increasing the adsorptive power of various kinds of charcoal by modifications in methods of carbonization, the most efficient of all charcoals being dense varieties derived from *cocoanut shells* and *fruit pits*. Canisters packed with such charcoal reduced the concentration of all toxic gases employed in the war (see Chapter XLII) below the danger limit. Toxic *smokes*, however, were not satisfactorily adsorbed. The explanation is similar to that advanced in a preceding chapter (p. 338) for the persistence of the fog obtained when a mixture of sulphur trioxide and oxygen is bubbled through water. The molecules of a gas are in such rapid motion that they are practically certain to strike the surface of the charcoal while passing through the canister, and to be adsorbed on this surface if the gas is easily condensible. The dimensions of the solid smoke particles, however, are much larger than molecular, and the par-

ticles are relatively stationary. Most of them, in consequence, are able to pass through the air channels between the charcoal granules without touching.

Pulverized charcoal, when shaken with a liquid, is also able to extract from it any dissolved substances, and to concentrate them upon its surface. Other finely divided materials, such as soil particles (p. 530), possess the same power of adsorbing substances from solution. Salts are, in general, only partially taken up; organic solutes are removed more completely. This property of charcoal is made use of in **water purification** and in **sugar refining** (p. 518). Charcoal is used, also, in making gunpowder, in reducing ores, and as a fuel (smokeless).

Coal. — When wood burns with a plentiful supply of oxygen, it gives nothing but carbon dioxide, water, free nitrogen, and a certain amount of ash (oxides and carbonates of the metals). What happens when it is heated in absence of oxygen, we have just seen. In nature, however, the intermediate case of slow decomposition of vegetable matter, *without* much heating and *without* access of oxygen, takes place on a large scale. Clay and sand, or even simply water, cover the vegetation and exclude the air, and the products are anthracite coal, bituminous coal, or peat. Little is known of the actual compounds contained in coal. We are concerned mainly with the products obtained by heating it in the absence of air, and with its use as a fuel.

Bituminous coals give much, and widely varying amounts, of volatile matter; anthracite coals give very little. The ash is the mineral matter of the original plants, with additional rock materials in some specimens. The coal is selected according to the purpose for which it is to be used. For coal gas, and even for coke, a variety high in volatile matter is chosen. For water gas (p. 426) anthracite or coke itself is employed.

Coal Gas. — The gas plant (Fig. 121) includes **(1)** the fire-brick retorts in which the coal is heated (externally) to 1300°, **(2)** the hydraulic main (a wide iron pipe) immediately above them in which most of the tar collects, **(3)** the condenser and wash box for cooling, condensing, and removing oils, **(4)** the

scrubbers (vertical and rotary) where the ammonia is taken out by water dripping over strips of wood and by stirring the gas with water, (5) the purifier where hydrogen sulphide is taken up by hydrated ferric oxide, and (6) the holder in which the gas collects.

The yield of gas varies considerably with the type of coal used. One ton of good *bituminous coal* should produce approximately 10,000 cubic feet of coal gas, 1300 pounds of coke, 5 pounds of ammonia and 12 gallons of tar. The average compo-
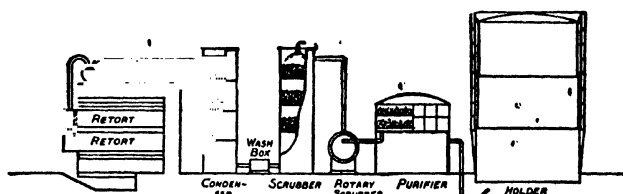
Fig 121.

sition of coal gas is: Illuminants 4 per cent, carbon monoxide 8 per cent, hydrogen 50 per cent, methane 29 per cent, ethane 3 per cent, carbon dioxide 2 per cent, oxygen and nitrogen 4 per cent.

The ammonia is made into ammonium sulphate. The tar may be used for road-making, as a waterproof material in building, and wherever pitch is applicable. More frequently it is separated by distillation, and other forms of treatment, and yields benzene C_6H_6, naphthalene $C_{10}H_8$, anthracene $C_{14}H_{10}$, phenol or carbolic acid C_6H_5OH and innumerable other valuable substances.

Coke Ovens. — The **by-product coke oven** is very much like the plant used for making coal gas. The difference is that the heating is arranged so as to decompose the volatile matter and cause it to leave as much as possible of its carbon behind. The resulting gas is consequently poor in illuminants, but excellent as a fuel. The ammonia and tar are also diminished in amount, but are still produced in paying quantities.

The **beehive coke oven** (Fig. 122), now largely discarded, is
a primitive device of fire-brick, shaped like a beehive. It is
simply filled with coal, part of which
is allowed to burn with a limited sup-
ply of air. It yields 66 per cent coke,
against 73 per cent from the by-
product oven. All the volatile mat-
ter, with its gas, ammonia, and tar,
escapes through an opening at the
top, where it burns in a large flame
and is wasted.
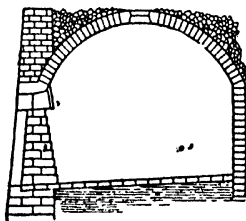
Fig. 122.

Properties and Uses of Coke. — Coke is a grey-black, hard
material of spongy texture. It burns without flame, and gives a
higher temperature than does coal, because no heat is used in
vaporizing moisture and volatile matter. On account of these
and other properties, it is used in immense quantities in reducing
ores of iron and other metals, and in smaller amounts in electric
furnace work and in making electric light carbons.

Coal as Fuel. — The quality of a fuel coal, and whether it is
worth its price, is learned by measuring its **calorific** (heating)
power. A sample (about 1 g.) is burned in a **bomb calorimeter.**
This is a closed, metal vessel, filled with oxygen and submerged
in a known weight of water. The coal is set on fire by a wire
heated electrically and, after it has burned, the increase in tem-
perature of the water is read off. Hence the heat in° calories
(p. 202) evolved by the burning of 1 g. of coal is obtained. In
engineering practice they use the number of British Thermal
Units (1 B.T.U. = heat required to raise 1 pound of water 1° F.)
developed by 1 pound of coal, and call the result the calorific
power. Since 1° C. = 1.8° F., the number of British Thermal
Units is evidently equal to 1.8 times the number of calories per
gram of coal.

	Calories per 1 g.	B.T.U. per 1 lb.		Calories per 1 g.	B.T.U. per 1 lb.
Hydrogen	28,800	51,840	Bituminous coal.	7,800	14,040
Charcoal (to CO_2).	8,080	14,544	Anthracite	8,000	14,400
Wood (seasoned)..	4,750	8,550	Petroleum	11,000	19,800

Knowing that 100 cal. will raise 1 g. of water from 0° C. to 100° C., and 540 cal. more will convert it into steam, it is possible to calculate how much steam should be furnished by 100 kilog. of coal of known heat of combustion. If the quantity falls short, then the furnace, draft, or method of firing may be defective. Too much draft, for example, merely introduces additional, useless air to be heated. Thus, if the flue gas, upon analysis, is found to contain, not 12 per cent carbon dioxide (normal), but only 3 per cent, then for every ton of coal burned, 52 tons of unnecessary air have been raised to the temperature of the furnace. By chemical tests, made in ways like this, the efficiency of every device in the modern factory is (or ought to be) controlled. If the coal is bought without heed to its calorific value, and used without experimental checks, the boiler house alone may easily waste the whole profit earned by the rest of the plant.

Source of the World's Energy. — The energy that does the world's work comes mainly from two sources; namely water power and the combustion of wood or of coal (which is fossil wood). The water comes from vapor, generated by the *sun's heat,* condensed as rain, and collected in lakes or reservoirs. The source of the energy of coal or wood is a little less obvious. When wood (which is largely cellulose) burns, it gives carbon dioxide, water, and heat. In fact, its combustion is represented by the equation at the foot of p. 513, *when the equation is read backwards.* Thus the sunlight, working through the machinery of the plant, takes the carbon dioxide and water, furnishes the energy (as light), and gives us wood and oxygen. And the wood and oxygen, when burned, give us back the original substances, and the equivalent of the original energy in the form of heat. Hence, our other main source of energy turns out to be the same as the first — the sun's rays — although the route by which the energy comes to us is a little less direct.

If, instead of *burning* the starch of the plant, *we consume it as food,* it goes through a *series* of changes instead of only *one.* But the end products are the same, namely, carbon dioxide and moisture issuing from our lungs, and heat and other forms of energy such as are developed in living organisms. Thus, whether

we use our muscles, a steam engine, or a waterwheel to do work, sunlight is in each case the ultimate source of energy employed.

Exercises. — 1. In fermentation, why does not carbon dioxide appear in bubbles *at once?*

2. How do we ascertain that acetic acid in aqueous solution is only slightly ionized? Give as many methods as possible.

3. (*a*) Why are charcoal and coke smokeless fuels? (*b*) Explain why bituminous coal burns with flames while anthracite does not.

4. Point out the analogies between the processes used in making coke and charcoal, and between their properties and uses.

5. A gas of sp. gr. 0.43 (air = 1) gives, on burning, 610 B.T.U. per cu. ft. How many B.T.U. is this per pound?

6. How many kilog. of steam, from water at 20°, can be made by burning 100 kilog. of coal, the heat of combustion of 1 g. of which is 8500 cal.?

7. What is "conservation"? What four industries or operations (or ways of performing operations) that are *wasteful* have been mentioned in this chapter (compare p. 379)?

CHAPTER XXXIX

ANIMAL LIFE AND ANIMAL PRODUCTS. FOODS

ONLY a few of the more important points in the chemistry of animal life and growth can be touched upon here. In the same way, the chemistry of **foods** is presented merely in outline. Some food products, derived from plants, have been described in earlier chapters. The single animal product dealt with in any detail in the present chapter is **soap**. In connection with soap, the subject of **colloids** is also briefly discussed.

Composition of the Human Body. — The following gives, roughly, the percentage of each element in the human body.

O	65	N	3	K	........0.35	Cl	......6.15	I ......trace
C	18	Ca	2	S	.........0.25	Mg	......0.05	F ....trace
H	10	P	1	Na	.......0.15	Fe 0.004	Si ....trace

We have already learned that the calcium and phosphorus are chiefly in the bones (p. 527). The nitrogen, sulphur, and iron are in the proteins. The sodium is largely present as salts, in the fluids of the body. The potassium is in the soft tissues and in special secretions like milk. As in the plant, the carbon, hydrogen, and oxygen are in the form of carbohydrates, proteins, and fats, and there is also much water.

Certain amounts of all these elements leave the system daily. Water evaporates from the lungs and skin. The carbon leaves in large amounts, chiefly from the lungs as carbon dioxide, and also as excreted fats, proteins and carbohydrates. Much of the nitrogen is eliminated, chiefly as urea $CO(NH_2)_2$. The salts are removed in the same way.

Animal Nutrition. — Since there is continual loss, there must be continual replacement. The animal resembles the plant in

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the fact that it can take up into its system *only dissolved material*. It differs from the plant, however, in the fact that it is provided with a wonderful laboratory in which insoluble substances are changed into soluble ones. This is the *digestive tract*, consisting of the mouth, stomach, and intestine. The production of soluble substances of suitable composition is called *digestion*.

The *processes* are too complex for detailed treatment here. Only a few typical *illustrations* can be given. The *principles* concerned have all been used and illustrated already, and many of the facts are contained in previous chapters.

Foods. — First, let us examine the table showing the percentage composition of the edible portion of several articles of food:

Food material	Water	Pro-tein	Fat	Carbo-hydrate	Ash
Beef (lean)	73.8	22.1	2.9	....	1.2
Cod	82.6	15.8	0.4	....	1.2
Eggs	73.7	14.8	10.5	....	1.0
Milk *	87.0	3.3	4.0	5.0	0.7
Butter	11.0	1.0	85.0	....	3.0
Cheese (cheddar)	27.4	27.7	36.8	4.1	4.0
Oatmeal	7.3	16.1	7.2	67.5	1.9
Wheat flour	11.9	13.3	1.5	72.7	0.6
Beans (dried)	12.6	22.5	1.8	59.6	3.5
Almonds	4.8	21.0	54.9	17.3	2.0
Maize (green corn)	75.4	3.1	1.1	19.7	0.7
Potatoes	78.3	2.2	0.1	18.4	1.0
Lettuce	94.7	1.2	0.3	2.9	0.9
Sugar	...	...	...	100.0	...

* The emulsified fat separates slowly as the cream; the protein (casein, colloidally suspended in the skim milk) is coagulated by rennet and constitutes cheese; the carbohydrates (lactose, a sugar) are then left in the water, along with inorganic salts.

We note, at once, that there is little more water in milk than in cod; that the animal foods, except milk, contain no carbohydrates; that potatoes and corn when dried are nearly all carbohydrate (starch); that lean beef when dry is nearly all protein; that some seeds (wheat and beans) contain almost no fat, some (oats) much more, and some (almonds and nuts) a very large amount; and that lettuce and other leaves are mainly water, with dissolved inorganic salts (valuable), contained in a light framework of cellulose (non-digestible).

Digestion of Starch. — The carbohydrates, in most foods which contain a large proportion of them, are mainly in the form of starch. The exceptions are milk, sweet fruits, and sugar itself. Starch is insoluble in water, and cannot be directly absorbed. But we have seen (p. 516) that, when boiled with a dilute acid, it is hydrolyzed, giving glucose. When bread and potatoes are masticated, an enzyme (p. 532), named ptyalin, contained in the saliva (alkaline), turns a part of it, by hydrolysis, into a soluble sugar, maltose. Later, in the small intestine, amylopsin completes this process. Here also another enzyme, maltase, splits the maltose into glucose. The glucose then passes through the intestinal wall and so goes into the circulation, where most of it is oxidized.

The *cooking* of starch (*baked* bread, *boiled* potatoes, etc.) breaks up the grains and makes the mixing with the enzyme more perfect and the digestion more rapid and complete.

Baking Powders. — The purpose of the powder is to generate carbon dioxide in the dough. The bubbles of the gas are retained by the sticky gluten of the flour. They expand when the dough is baked, and give to it the open texture which, when the bread is eaten, facilitates access of the saliva to every particle.

Baking soda $NaHCO_3$, if used alone, will give off, when heated, half the carbon dioxide it contains (p. 491). The sodium carbonate which remains in the bread, however, has an acrid taste. By its action on the gluten in the flour, it gives also a yellow color and an unpleasant odor. Finally, the carbonate of soda tends to neutralize the gastric juice (acid) of the stomach and so to interfere with digestion.

To obviate these difficulties sour milk (containing lactic acid) is sometimes used in making the dough. Occasionally vinegar (p. 534) is added. Most frequently a baking powder, containing an acid substance along with the soda, is employed. The acid substances contained in baking powders are alum (p. 585), acid-phosphate of calcium or sodium, or potassium-hydrogen tartrate. The last, known commonly as **cream of tartar** $HKC_4H_4O_6$, acts as follows:

$$HKC_4H_4O_6 + NaHCO_3 \rightarrow NaKC_4H_4O_6 + H_2CO_3 \rightarrow H_2O + CO_2.$$

The sodium-potassium tartrate which remains is better known under the name of *Rochelle Salt.*

It is important that the soda and the acid substance should be used *in the correct proportions,* which can be calculated from the equation. In commercial baking powders a little corn-flour is added, to keep the particles of the other compounds apart and prevent that gradual interaction which otherwise would be bound to occur. The acid substance should also be somewhat insoluble, so that, even when wet, it will not act upon the soda until ample time has been allowed for complete mixing with the dough.

Bakers' Bread. — The "raising" of bakers' bread is effected by adding yeast. The batch is "set" in a warm place for some hours to permit the yeast to propagate and to act upon the sugar in the flour. In this action, as we have seen (p. 532), carbon dioxide and alcohol are produced. A little sugar, molasses, or malt extract is added to the dough, to afford a larger supply of the sugar required for the production of the carbon dioxide.

The whites of eggs "raise" cake, without the presence of any soda, because of the expansion under heat of the bubbles of air entangled with the albumen when the eggs are "whipped."

Fats and Oils. — The fats and oils found in the bodies of animals, or pressed from the seeds of plants, are composed mainly of various esters (p. 437). As such, they are formed by the inter-action of a tribasic alcohol, **glycerine** $C_3H_5(OH)_3$, with higher acids of the paraffin and olefine series of hydrocarbons, such as the saturated acids $C_{15}H_{31}.COOH$ **(palmitic acid)** and $C_{17}H_{35}.COOH$ **(stearic acid),** and the unsaturated acid $C_{17}H_{33}.COOH$ **(oleic acid).** For example:

$$C_3H_5(OH)_3 + 3H(COO.C_{15}H_{31}) \rightleftarrows C_3H_5(COO.C_{15}H_{31})_3 + 3H_2O.$$

glycerine   palmitic acid   glyceryl palmitate
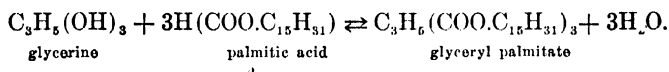
The glycerine esters of the saturated acids are solid at ordinary temperatures (fats), while those of the unsaturated acids are liquid (oils). **Beef suet** is a mixture of about three-fourths glyceryl palmitate (palmitin) $C_3H_5(CO_2C_{15}H_{31})_3$ and glyceryl

stearate (stearin) $C_3H_5(CO_2C_{17}H_{35})_3$, and one-fourth glyceryl oleate (ólein) $C_3H_5(CO_2C_{17}H_{33})_3$. **Hog lard** contains about 40 per cent of the former and 60 per cent of the latter, and is therefore softer. **Butter** includes the same esters, with about 14 per cent of water. When butter is dried, the remaining fat contains about 8 per cent of glyceryl butyrate (butyrin) $C_3H_5(CO_2C_3H_7)_3$. **Olive oil** contains 75 per cent of olein. **Cotton seed oil** is similar in nature.

All these fats and oils contain, also, a small amount of the *free acids*. They must not be confused with *mineral oils* like petroleum, which are mixtures of hydrocarbons.

Oleomargarine is an artificial butter. It is made by straining melted beef fat and allowing it to stand at 24°. Much of the stearin crystallizes out and the remaining liquid (the "oleomargarine") is pressed out and allowed to solidify. The solid is finally mixed with a little of some oil, to render it softer, and is churned with milk to impart the proper flavor. Although it lacks the butyrin, the product is similar in chemical nature to butter, and just as nutritious and wholesome.

Hydrolysis of Fats and Oils. — The chief chemical property of the fats and oils, and in fact of all esters, is that each can be *decomposed*, or hydrolyzed, to give back the alcohol and acid from which it is derived. Thus, when ethyl acetate is boiled with water, it is slowly decomposed into ethyl alcohol and acetic acid:

$$C_2H_5(CO_2CH_3) + H_2O \rightarrow C_2H_5OH + HCO_2CH_3.$$
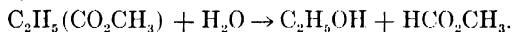
In the case of the fats and oils, if water alone is used, they must be heated in a closed vessel, or autoclave, under pressure so as to secure a high temperature (about 200°):

$$C_3H_5(CO_2C_{15}H_{31})_3 + 3H_2O \rightarrow C_3H_5(OH)_3 + 3HCO_2C_{15}H_{31}.$$
$$\text{palmitin} \qquad\qquad\qquad \text{glycerine} \qquad \text{palmitic acid}$$
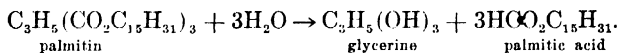
When the mixture has cooled, the acid, which is insoluble in water, forms a solid cake, while the glycerine is dissolved in the water.

With water alone as a hydrolyzing agent, however, the reaction is slow and incomplete and, at the high temperatures which it is necessary to employ, some destruction of fatty matter is apt

to occur. In the presence of dilute sulphuric acid as a catalyst, the hydrolysis can be carried out much more satisfactorily and rapidly, even at 100°. Sulpho-derivatives of the fatty acids are still more effective as catalysts, since they are freely soluble both in fats and oils and in water, and hence promote the miscibility of the two layers (**Twitchell process**).

When tallow (beef fat) is treated in this way, the product is a mixture of palmitic, stearic, and oleic acids. The latter, being liquid, is pressed out, and the solid material is used with paraffin in making candles. The glycerine is separated from the water and used in making nitroglycerine (p. 596) and in medicine.

Hydrogenation of Oils. — The market value of solid fats is much higher than that of liquid oils. Many natural oils, indeed, possess disagreeable characteristics (taste, odor, etc.) which render them totally unsuitable for edible purposes. They may be converted into more appetizing edible fats, however, by *hydrogenation.* At 200°, in the presence of finely divided nickel as a catalyst, these unsaturated compounds take up hydrogen and become saturated, the oil *hardening* to a fat in the process.

Many substances which were formerly waste products, such as cotton-seed oil, are now treated in enormous quantities in this way. The hydrogenation of low grade oils (for example, fish oil) is also of great industrial importance in the manufacture of **soap** (see p. 551) and **candles.**

Digestion of Fats. — At body temperature, the fats and oils present in foods are all insoluble in water, and therefore cannot be directly absorbed into the system. But fats, if already emulsified (p. 138), as in milk, are hydrolyzed by a **lipase** (enzyme for *fat*) in the gastric juice of the stomach, and are decomposed into the acid and glycerine (p. 546)   Fat in larger masses is hydrolyzed by lipases in the bile and here the acid (insoluble in water) is dissolved. The acid and the glycerine then diffuse through the intestinal wall and finally recombine to form fat in the blood. Some of this fat is deposited in the tissues and some is oxidized (giving muscular energy and heat).

Cooking (application of heat) does not affect the digestibility of fat. However, when fat is heated too strongly, the beginning

of destructive distillation produces unsaturated compounds. These are intensely irritating to the digestive organs — as the way their vapors bring tears to the eyes would lead us to expect.

Digestion of Proteins. — The proteins contained in foods, of which the white of an egg (albumen) is a typical example, are not affected by saliva, but, when mixed with the gastric juice of the stomach, they are changed by the free hydrochloric acid it contains into **syntonin.** This in turn is hydrolyzed by the **pepsin** (enzyme), also contained in the gastric juice, into **peptones** which are soluble in water. These changes, only partly carried out in the stomach, are completed in the small intestine by the **trypsin** of the pancreatic juice, and the peptones (or amino-acids into which they are split) pass through the intestinal wall into he circulation. The **casein** of milk, being in colloidal suspension, s completely hydrolyzed to peptones in the stomach.

When heated, as in *cooking*, the proteins do not behave like. Some, like albumen (white of egg) become coagulated, though probably *nct* less digestible. The same is true of the blood proteins (hæmoglobin, etc.) of beef. On the other hand, the connective tissue of meat (chiefly **collagen**) is insoluble in cold water, but in hot water goes into colloidal suspension as **gelatine.** It is therefore softened by judicious roasting (under-done meat), provided the operation is not carried so far (over-done meat) that the water in the meat is largely evaporated.

Fuel Value. — While food is needed primarily to replace the material which is continually eliminated from the system, the organism also requires energy to maintain the routine motions of the heart, intestines, lungs, and other organs, and the normal muscular tension, as well as the movements of the muscles in walking and working. If the heat derived from routine changes is not sufficient to maintain the temperature (37° C.) of the body, then additional food material is oxidized by the system for this specific purpose (compare p. 197). The values of foods are therefore conveniently estimated in terms of the heat they produce when burned — their **fuel values.**

The average fuel values, as measured in the calorimeter, with

certain necessary corrections, and expressed, as is usual in this work, in **large calories*** *per gram*, are: Carbohydrates 4 Cal., fats 9 Cal., proteins 4 Cal. The fuel values *per pound* (= 453.6 g.) are 453.6 times greater: Carbohydrates 1800 Cal., fats 4080 Cal., proteins 1800 Cal.

Normal Diet. — There is much uncertainty, as yet, in regard to the best choice of foods, in respect to the exact distribution in kind and quantity. We know, however, that life cannot be maintained on one kind (say sugar or gelatine) alone. A mixed diet is necessary. In general, it appears that 100 g. of proteins (giving 4 × 100 Cal.) per day, and a sufficient amount of other foods to bring the total fuel value up to 2200 Cal. per day, is sufficient for a person leading a strictly sedentary life. For work involving physical exercise, larger values, up to about 3800 Cal., are required.

From the data given in the table (p. 543) the fuel value of 100 g. of each kind of food can easily be calculated.

Fuel Values and Prices of Foods. — If the current prices are considered, one can also readily calculate the fuel value obtainable for a given sum of money invested in each kind of food. Thus: lean beefsteak contains 22.1 per cent of protein, or 0.221 pounds per pound of meat. The fuel value of this protein is 0.221 × 1800, or 398 Cal. per pound.

	Price * per 1 Pound, Cents	Fuel Values per 1 Pound				Cal. per 10 Cents
		Protein	Fat	Carbohyd.	Total	
Steak	25	398	118	....	516	206
Eggs	24	266	428	....	694	290
Oatmeal	5	290	294	1215	1799	3600
Flour	5	249	61	1309	1619	3240
Almonds	40	378	2240	311	2929	732
Potatoes	2.5	40	4	331	375	1500
Cheese	25	500	1500	74	2074	830
Sugar	5	...	....	1800	1800	3600

* The prices vary greatly with the quality, the season of the year, the demand, the supply, etc.

* One large calorie (1 Cal.) is equal to one thousand small calories (1000 cal.), as hitherto defined (p. 72) and used.

Vitamins. — A diet may be carefully balanced with respect to carbohydrates, fats and proteins, and yet lead to malnutrition through deficiency in *vitamins*. These are substances present in minute quantities in most fresh or unsterilized foods, particularly in milk and green vegetables, without the aid of which certain parts of the animal mechanism either cease to develop or fail to perform their functions entirely. The three known types are:

(1) **Fat-soluble vitamin A,** plentiful in milk, butter, the yolks of eggs, cod-liver oil and the leaves of green plants, but not found in grains, sugars, or refined vegetable fats and oils. This vitamin is needed to promote the growth of children; its absence leads to rickets and a disease of the eye called xerophthalmia.

(2) **Water-soluble vitamin B,** plentiful in the *outer hull* of grains, beans, green leaves and fruit and yeast, but not in the *kernels* of grains, such as polished or milled rice. Deficiency of this vitamin in the diet leads to boils and skin eruptions, and in extreme instances to beriberi.

(3) **Water-soluble vitamin C,** plentiful in citrous fruits, tomatoes, cabbage, lettuce and other fresh fruits and vegetables. The value of this vitamin lies in the prevention and cure of scurvy. It is easily destroyed, except in the case of acid foods, by heating, drying or aging. Since milk is *neutral*, infants fed entirely on *pasteurized milk* are almost sure to develop a mild case of scurvy unless the diet also includes a little orange juice or some other source of water-soluble vitamin C. Owing to the acid nature of tomatoes, even the canned product is rich in this vitamin. A knowledge of this fact was put to good use by the authorities of the British armies in Mesopotamia and Palestine during the war, when fresh fruits and vegetables were unobtainable.

Animal Products. — Many valuable products, apart from foods, are derived from animal life. The use of animal products in *fertilizers* (calcium phosphate from bones, nitrogen compounds from manure, etc.) has already been discussed (Chapter **XXXVII**).

When bones or dried blood are subjected to destructive distillation (compare p. 535), the residue consists of animal•charcoal. The charcoal from bones (bone black) contains 90 per cent of mineral matter, largely calcium phosphate, and only 10 per cent of carbon. Animal charcoal, being a very active adsorbent (p. 536), is used in sugar refining.

The basis of wool, and of hair fibers in general, is a protein called keratin. The silk fiber is also of animal origin, but differs very widely from wool in its structure and properties. As spun by the silkworm in the preparation of its cocoon, it consists of two filaments composed of a protein called *fibroin* surrounded and cemented together by a gluey substance known as *sericin* or silk-gum.

Glue, an impure form of gelatine (p. 548), is obtained from the skin and bones of animals by extraction with water under pressure. Leather is prepared from the hides by tanning (see p. 680).

Casein, a protein contained in milk and precipitated therefrom by dilute acids, has recently found many interesting applications. In the modified form of cheese, of course, it has long been of value as a food. Mixed with various alkalies it gives *glues, cements* and *putties*. It is used as an ingredient in *paints,* and for *sizing* or *enameling* paper. Paper bottles are made waterproof by impregnating them with casein and then exposing them to the vapor of formaldehyde (p. 436). *Galalith* (milk-stone) is a plastic harder than celluloid (p. 595) and non-inflammable, made by the same hardening action of formaldehyde on casein.

Soap. — When fats are hydrolyzed by heating with a solution of *caustic soda* NaOH, instead of water, *the sodium salts of the acids are obtained.* These sodium salts are known as soaps and the operation is called saponification:

$$C_3H_5(CO_2C_{15}H_{31})_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3Na(CO_2C_{15}H_{31})$$

palmitin   glycerine   sodium palmitate (a soap)
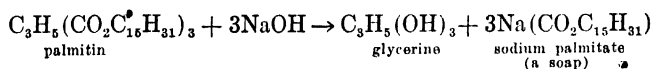
The sodium palmitate or other soap is soluble in the water. When common salt is added, however, the soap coagulates and separates into a floating layer which solidifies on cooling.

Soft soap is made with potassium hydroxide, and is composed of the potassium salts of the organic acids.

Manufacture of Soap. — Soap is made in large iron caldrons. These contain closed steam coils for heating, and pipes delivering live steam, when needed, for stirring the mass. The fat is mixed with caustic soda solution containing, at first, only about one-fourth of the total amount of the base that the above equation requires. When, after heating and stirring, a uniform mixture has been produced, the rest of the alkali is added gradually and the heating is continued until the reaction appears to be complete. Salt is now dissolved in the mixture and the soap separates as a curd. The curd floats, leaving the "spent lye," containing the salt solution and much of the glycerine, in the lower layer. This process is called **salting out.**

When the process stops at this point, the upper layer is known as **curd soap,** and may be dipped out and allowed to cool and solidify. Most "Marseilles" soaps are curd soaps made in this way. A large part of the imported "Castile" soaps are of the same kind.

Curd soaps contain salt, glycerine, adhering lye, and other impurities. To prepare a purer soap, the spent lye is run off, dilute brine is added to the soap, and the curd and brine are stirred up. When separation has again occurred, the brine is run off and the process repeated. Finally, some water is added, and steam is run in until the curd mixes completely with the water. When the solution stands, it "settles," that is, resolves itself once more into two distinct layers. The upper layer is called **settled soap.** The washing with brine and temporary dissolving in water remove the impurities, and hence settled soap is the purest variety. The greater part of the soap made in the United States and in Great Britain is of this kind.

The qualities of soaps are varied by adding "fillers," such as sodium carbonate, borax, or sodium silicate. **Soap powders** are often made of ground soap mixed with sodium carbonate. Dyes and perfumes are sometimes added to soaps. Air bubbles are mixed with the soap, by beating, to give the floating varieties. Soap for scouring contains fine sand. Transparent soaps are made by dissolving the soap in alcohol, or by the addition of glycerine or sugar.

Chemical Properties of Soaps. — The soaps, being sodium salts, dissolve in water and have the *usual properties of salts*. Thus, when an acid is added, double decomposition takes place:

$$Na(CO_2C_{15}H_{31}) + HCl \rightarrow NaCl + H(CO_2C_{15}H_{31}) \downarrow.$$

sodium palmitate   palmitic acid
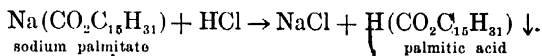
The *acids*, being insoluble, are thrown down, as white precipitates.

When other salts are added, similar actions occur. Thus with calcium chloride solution, calcium palmitate is precipitated:

$$2Na(CO_2C_{15}H_{31}) + CaCl_2 \rightarrow 2NaCl + Ca(CO_2C_{15}H_{31})_2 \downarrow.$$
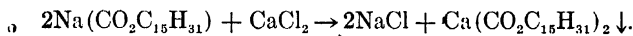
This action is important in connection with "hardness" in water (p. 502).

Colloidal Suspension. — We have seen (pp. 138, 516) that starch can be suspended in water in such a fine state of division that the liquid is transparent, and *runs through a filter* without leaving any solid on the paper. Yet this "suspension" lacks some of the characteristic properties of a solution.

The simplest proof that this is a case of imitation solution, and not of true solution (molecular dispersion, p. 138), is obtained by examining the liquid with the ultra-microscope. A converging beam of strong light is sent through the liquid *horizontally* (Fig. 123), and the illuminated place is viewed *from above* through a microscope. When the room is dark, and the only light comes from the horizontal beam, a colloidal suspension shows minute points of light. A true solution — such as one of common salt or of alcohol — remains perfectly dark. The points of light are produced by myriads of *suspended particles*, which although extremely minute,

FIG. 123.

are of far larger than molecular dimensions. Solutions of soap, gelatine, and many dyes, blood serum, and innumerable other liquids contain such suspended particles.

The particles of a colloid (like starch), when viewed in this way, show a continual, unordered, zig-zag movement (Brownian
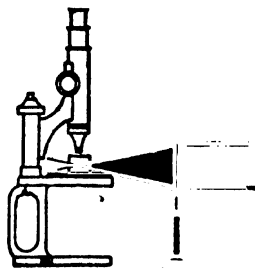
movement), which is more rapid the smaller the particles, and is due to the impacts of the molecules of the solvent.

Other Properties of Colloidal Suspensions. — The freezing-point, boiling-point and vapor pressure of a liquid containing a colloid in suspension are all practically *identical* with those of the pure solvent. This is quite different from what we have seen to be the case with true solutions (p. 153), and indicates that the fraction of the "solute" particles present is substantially *zero*. The unit particles of suspended material, indeed, are complex aggregates so much larger than the ultimate molecules into which true solutes are broken up that the number of them present, compared with the number of solvent molecules, is entirely negligible.

When a "solution" of a colloid is placed in a "diffusion-shell" of parchment, surrounded by pure water, *none of the colloid escapes* through the minute pores of the shell. Ordinary, non-colloidal solutes do escape, more or less rapidly (salt rapidly, sugar slowly, see p. 522). In this way a *mixture of colloid and non-colloid* (say, starch and salt) *can be separated*, if the water surrounding the shell is replaced by pure water at intervals until all the non-colloid has been removed. This method of separation is called **dialysis**.

Finally, matter in colloidal suspension may be *coagulated* (or flocculated) by addition of electrolytes or certain other colloids, *and is then precipitated*.

Colloidal Matter in Soap Solutions. Explanation of Salting Out. — Soaps, being salts of weak acids, are somewhat hydrolyzed in solution. Letting R stand for the hydrocarbon part of the acid radical.

$$Na(CO_2R) + H_2O \rightleftarrows H(CO_2R) + NaOH.$$
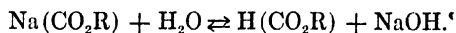
The free acid HCO_2R thus produced combines with the original salt $NaCO_2R$ to form an acid salt $NaH(CO_2R)_2$. *This acid salt exists in colloidal suspension in the soap solution*, in equilibrium with the ions and molecules of the original salt and the NaOH.

The capacity for being coagulated and precipitated, which is characteristic of colloidal matter, is shown very clearly by soap

solutions. Most *sodium salts will coagulate a soap solution* and precipitate the soap as a curd. The acid salt $NaH(C_2O_2R)_2$ seems to collect (**adsorb**) and carry down with it the most of the sodium hydroxide. As both of the substances on the right of the equation (above) are thus precipitated, the equilibrium is displaced to the right, and the precipitation becomes complete. This explains the process of "salting out ' (p. 552) which plays so large a part in the manufacture of soap.

" **Causes of the Cleansing Action of Soap.** — The chief use of soap solution is in removing grease and dirt from yarn, cloth, or clothing, and from woodwork and kitchen utensils. Soap solution has *two* more or less distinct properties, *one* of which enables it to remove oil or grease (viscous, insoluble liquids), and the *other* of which enables it to remove dust and dirt (largely minute, solid particles of carbon — soot). The former is its *emulsifying power*, the latter is probably connected with its nature as a *colloidal suspension*.

The Emulsifying Action of Soap. How Soap Removes Grease. — When an insoluble oil, such as kerosene or lubricating oil, is shaken with water it is divided into minute droplets separated by water from one another. When the shaking ceases, however, the droplets begin to run together and soon the oil and water have separated once more into two layers of transparent liquid. When very dilute soap solution and oil are shaken together, however, the droplets do not run together, but remain permanently suspended. The mixture is opaque and more or less viscous. Such a **permanent mixture of two insoluble liquids** is called an **emulsion** (compare p. 138).

Soap solution, when *rubbed* on oily or greasy goods, *emulsifies the grease,* converts it into droplets, surrounded by soap solution and separated from the cloth, and so permits it to be washed off.

In mayonnaise dressing, which is a thick, almost solid, permanent emulsion, the olive oil is emulsified by the colloidal matter of the yolks of the eggs which have been beaten into the vinegar.

How Soap Removes Dirt. — When a solution containing colloidal substances, such as many dyestuffs and organic coloring matters, is shaken with finely pulverized charcoal, the colloidal substance adheres to the surface of the powder (is **adsorbed**) and the liquid is consequently decolorized (see p. 537).

When dilute soap solution is shaken with diatomaceous earth and the mixture is filtered, the clear liquid is found to have been deprived of the soap. The soap is evidently precipitated (adsorbed) on the surface of the particles of the solid.

Clearly there is a tendency to cohesion between the colloid in a soap solution and the particles of a fine powder. When there is much of the powder, and little of the soap in solution, the powder takes the soap out of the solution? When, however, there is much of the colloid in the form of soap solution, and little of the solid, and that very finely divided, the same tendency to adsorption exists, *only, in this case, the colloidal particles carry off the powder.* In short, the dirt is removed by adsorption into the solution.

Possible Objections to the Foregoing Explanation. — Formerly soap solution was supposed to remove grease (and soot?) because of its slight alkaline reaction, due to hydrolysis. This explanation must be given up because: (1) an alkali so dilute that it exists in equilibrium with the free fatty acid, cannot possibly saponify the *ester* contained in a grease spot. (2) Pure alkali of the same concentration (or stronger) has no more emulsifying power than water. Such an alkaline solution will indeed emulsify an animal or vegetable oil (cod-liver oil, cotton oil, castor oil), but it does so by interacting with the free fatty acid always present in such oil (p. 546) and *forming therefrom a soap.* Such an alkaline solution does *not* emulsify kerosene, although soap solution does. The emulsifying agency is always a soap. (3) Very dilute alkali has no more effect upon soot than has water — but soap solution takes clean (greaseless) soot instantly into permanent suspension.

The power of forming an emulsion depends, theoretically, **upon** the *abnormally low surface tension* of dilute soap solution.

Very dilute alkali has the same high surface tension as has pure water.

Exercises. — 1. Make equations for the formation: (*a*) of maltose from starch; (*b*) of glucose from maltose.

2. Make a connected statement showing the stages in the digestion of milk.

3. Why does fat appropriately form a larger proportion of the diet in the Arctic regions than elsewhere?

, 4. Give the weights of carbohydrate, protein, and fat which would supply a menu, such that the total food value was 3000 Cal., and that 100 g. of protein was included, and the remaining fuel value was divided equally between carbohydrates and fats.

5. Calculate the calorific value of 1 kilog. of: (*a*) wheat flour, (*b*) oatmeal.

6. (*a*) In what proportions by weight should baking soda and cream of tartar be used in raising bread? (*b*) What is the objection to using too large a proportion of baking soda? (*c*) Why must baking powder be kept in a dry, cool place?

7. Why does vinegar liberate carbon dioxide from baking soda? Make the equation for the action.

8. Make equations for the formation of: (*a*) ethyl formate; (*b*) glyceryl formate; (*c*) ethyl stearate.

9. Make equations for the action of superheated water on: (*a*) stearin, and (*b*) olein; and for the action of caustic soda on: (*c*) stearin, and (*d*) ethyl acetate.

10. Summarize the facts which show soaps to be salts.

11. (*a*) Write the full equation for the hydrolysis of sodium palmitate. (*b*) What reaction (acid or alkaline) should soap solution possess, and why (p. 326)?

12. Why does "French dressing" (vinegar, salt, and olive oil) give an emulsion, which is much less durable than mayonnaise dressing?

CHAPTER XL

MAGNESIUM AND ZINC. IONIC EQUILIBRIA CONSIDERED QUANTITATIVELY

WE may now return to the consideration of the metals, which was interrupted after the metals of the alkaline earths had received attention. The remaining elements of the third column of the periodic table, namely **glucinum** (Gl, at. wt. 9.1), **magnesium** (Mg, at. wt. 24.32), **zinc** (Zn, at. wt. 65.37), **cadmium** (Cd, at. wt. 112.40), and **mercury** (Hg, at. wt. 200.6), although all **bivalent**, do not form a coherent family. Glucinum and magnesium resemble zinc and cadmium, and differ from the calcium family, in that the sulphates are soluble, the hydroxides easily lose water, and the metals are not rapidly rusted in the air and do not easily displace hydrogen from water. They resemble the calcium family, and differ from zinc and cadmium, in that the sulphides are hydrolyzed by water, the oxides are not reduced by heating with carbon, and the metals do not enter into complex ions (p. 606). But glucinum differs from magnesium and resembles zinc in that its hydroxide is acidic as well as basic. This is not unnatural, since in the periodic system it lies between lithium, a metal, and boron, a non-metal.

Mercury is the only member of the group that forms two series of compounds. These are derived from the oxides HgO and Hg₂O. Mercury approaches the noble metals in the ease with which its oxide is decomposed by heating, and in the position of the free element in the electromotive series. The other members of the present group are all well above hydrogen in this series (see p. 240), and displace hydrogen from dilute acids. In deference to its abnormalities, we shall postpone the discussion of mercury to a later chapter, where it will be taken up in conjunction with copper, an element which resembles it most closely in its chemical relations.

Glucinum occurs in beryl, a metasilicate of glucinum and aluminium $Gl_3Al_2(SiO_3)_6$. Beryls, tinted green by the presence of a little silicate of chromium, are known as **emeralds.** The element is exceedingly rare, and its compounds are not of sufficient importance to warrant extended consideration.

MAGNESIUM Mg

Occurrence. — Magnesium carbonate is found in **dolomite** $CaCO_3,MgCO_3$, a common rock, and in small amounts as **magnesite** $MgCO_3$. The sulphate and chloride are found at Stassfurt. Several natural silicates of magnesium, such as **meerschaum, asbestos, talc** or **soapstone,** and **olivine,** are familiar minerals.

Asbestos, a fibrous material, is used in making fireproof cloth and cardboard. Soapstone is made into sinks and table tops for use, for example, in laboratories.

The Metal Magnesium. — The metal is made by electrolyzing a molten mixture of magnesium, potassium, and sodium chlorides. A carbon rod forms the anode, and the iron crucible the cathode, on which the metal collects in globules. The mass, when cold, is broken up and the metal is recast in bars. The metal can be drawn, through a die, into ribbon or wire.

Magnesium *rusts* in the air, gradually crumbling to a white powder of a basic magnesium carbonate. It *burns* in air, with a brilliant white light, producing a mixture of the oxide MgO and nitride Mg_3N_2 (see argon, p. 376). Magnesium filings, mixed with potassium chlorate, give **flash-light powder.** Signal lights are made of shellac, barium nitrate and magnesium powder.

Oxide MgO and Hydroxide $Mg(OH)_2$. — The **oxide** is made by heating magnesium carbonate, and is therefore called **calcined magnesia.** Being very infusible ("refractory") it is used in lining electric furnaces. On account of its poor heat conductance, it is also employed very extensively for insulating pipes and boilers, and so reducing heat losses (85% **Magnesia**). It combines slowly with water, giving the **hydroxide** $Mg(OH)_2$, which with water gives a mortar that hardens under the action

of the carbon dioxide of the air (see mortar, p. 500). The oxide is *basic*, and with acids gives salts by double decomposition.

Magnesium hydroxide $Mg(OH)_2$, being insoluble, is easily precipitated by adding sodium hydroxide to a solution of a salt of magnesium. When moistened and mixed with a little magnesium chloride, it sets to a hard basic chloride of variable composition. The mixture, to which sawdust is sometimes added, is used as a plaster in house decoration.

Magnesium hydroxide is **not** precipitated by addition of ammonium hydroxide to a solution of a magnesium salt *when salts of ammonium are also present in quantity in the solution*. The reason for this will be developed later on in the chapter (pp. 566-569).

Salts of Magnesium. — **Magnesium carbonate.** $MgCO_3$ is found in nature. That made by precipitation is a basic carbonate $3MgCO_3,Mg(OH)_2$, **magnesia alba**, which is used in tooth powder and for polishing silver.

Magnesium sulphate $MgSO_4$ is commonly sold as the heptahydrate, $MgSO_4,7H_2O$, **Epsom salt**. It is found in the salt deposits and in many aperient mineral waters. Thus **Hunyadi water** contains little beside 47 g. Epsom salt and 52 g. sodium sulphate $(Na_2SO_4,10H_2O)$ and 1 g. sodium bicarbonate per liter. The salt is used for loading cotton goods and as a purgative.

Magnesium chloride $MgCl_2$ is found in sea water and in some natural waters. It occurs in the Stassfurt deposits, alone, and as **carnallite** $MgCl_2,KCl,6H_2O$. The latter is a most important source of potassium chloride (p. 528), and almost all the magnesium chloride combined with it is thrown away. Magnesium chloride is very deliquescent (p. 154) and, being present in impure table salt, causes the latter to cake or even become moist in damp weather. Addition of a very little sodium bicarbonate to the salt remedies this difficulty. Magnesium chloride is a very objectionable form of hardness in water, because hot water partially hydrolyzes the salt and liberates hydrochloric acid, which attacks and corrodes the iron of the boiler and tubes. Hence sea water cannot be used in marine boilers.

The only **phosphate of** importance is ammonium-magnesium

orthophosphate $NH_4MgPO_4,6H_2O$, which appears as a crystal-line precipitate when sodium phosphate and ammonium hydroxide (and chloride, p. 560) are mixed with a solution of a magnesium salt.

Analytical Reactions of Magnesium Compounds. — The magnesium ion is colorless and bivalent. Soluble carbonates precipitate basic carbonates of magnesium, but not when ammonium salts are present. The latter limitation distinguishes compounds of magnesium from those of the calcium family. Sodium hydroxide precipitates the hydroxide of magnesium, except when salts of ammonium are present. The mixed phosphate of ammonium and magnesium, in presence of ammonium hydroxide, is the least soluble salt.

ZINC Zn

Chemical Relations of the Element. — Zinc is bivalent in all its compounds. Of these there are two sets — the more numerous and important one, in which zinc is the positive radical ($Zn.SO_4$, $Zn.Cl_2$, etc.), and a less numerous set, the zincates, in which zinc is included in the negative radical ($Na_2.ZnO_2$, etc.). Zinc is the first of the metals which we have, so far, studied in detail to exhibit compounds of this latter type. Many other metals, however, will be found to behave similarly in subsequent chapters (compare p. 581). Both sets of salts are hydrolyzed by water, as the hydroxide is feeble whether it is considered as an acid or as a base. The salts are all **poisonous.**

Occurrence and Manufacture. — Zinc is found in nature mainly as **zinc blende** ZnS (in large amounts in Missouri) and **smithsonite** $ZnCO_3$ (Spain and U. S.).

In the case of the carbonate ore, the oxide ZnO is first obtained by heating. When zinc blende ZnS is the ore, it is crushed and pulverized, concentrated by flotation (see p. 603), and then roasted (p. 332) to remove the sulphur and leave the oxide:

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$
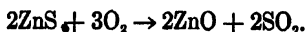
The ore is fed in at the top of a huge, box-like furnace (Fig. 124 diagrammatic) through which rush the flames and heated gases from fuel gas burning with an excess of air. The ore is turned over and gradually displaced forward by moving rakes until, at the end, it drops to the next level. Here it is raked in the opposite direction, until it falls
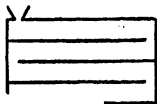
FIG. 124.

to the third level. ' The ore collects at the bottom fully oxidized, while the sulphur dioxide in the gases is made into sulphuric acid. The oxide from either ore is then reduced by heating with powdered coal:

$$ZnO + C \rightarrow Zn + CO.$$
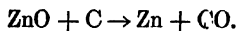
This treatment of zinc ores should be carefully considered. Since ores of most metals consist of the carbonate, sulphide, or oxide of the metal, these steps are common to most metallurgical processes. In the case of other metals, only the forms of the furnaces and other details vary.

In the case of zinc, because it is a *volatile* metal, the heating of the mixture of oxide and coal is conducted in *retorts,* from which the metal issues as *vapor.* The mixture is placed in fire-clay cylinders (4 to 5 ft. long), which are arranged in several tiers in an oblong, gas-heated furnace (Fig. 125). A fire-clay receiver is luted on with clay. The carbon monoxide burns with a blue flame at the nozzle of each receiver, while the zinc condenses to liquid within it. From time to time the liquid metal is raked out into a traveling iron pot, from which it is poured into moulds.

The world's production of zinc in 1921 amounted to 440,000 metric tons. In 1916, stimulated by war requirements, the production was in excess of 1,000,000 metric tons.

Properties and Uses. — The metal is *silvery* and crystalline. At 120 to 150° it can be rolled into sheets between hot rollers, at 200 to 300° it becomes brittle, at 419° it *melts,* and at 950° it *boils.* The *density* of the vapor shows it to be monatomic. Zinc vapor *burns* with a bluish flame, giving ZnO. In air the metal

does not rust, being protected by a non-porous coating of a basic carbonate which adheres closely to the surface.

Sheet zinc is used for gutters and cornices. Iron is coated (galvanized) with zinc by thorough cleaning with dilute sulphuric acid or the sand blast, and dipping in melted zinc. Iron netting, corrugated iron for sheds and roofing, and iron gutters, tanks, and pipes are coated with zinc, either in this way, or by electroplating (see p. 624). Sherardized iron is made by covering the article with zinc dust and baking it. The zinc protects the iron, primarily because it excludes the air from the surface, and secondarily because, even when the coating is broken, the zinc, being the more active metal of the two (p. 64) is rusted
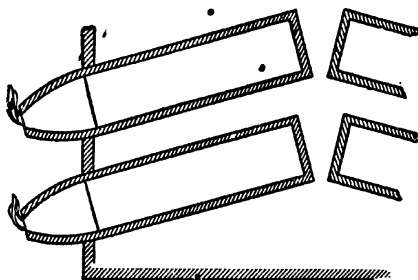
Fig. 125.

first. Zinc is used also in extracting silver from crude lead (p. 158), as the active metal (anode) in batteries, and in several alloys (e.g. Babbitt's metal, p. 475, brass, and German silver). In the laboratory granulated zinc, made by pouring the melted metal in a thin stream into water, and zinc dust (impure, contains ZnO), are the forms commonly employed.

Zinc Chloride ZnCl$_2$ — The chloride is formed in the action of zinc or zinc oxide on hydrochloric acid. It is a white, deliquescent solid. Its aqueous solution *gelatinizes cellulose* and *dissolves it* (p. 514), and thus is used in parchmentizing paper and in impregnating wood to prevent decay. The aqueous solution is acid (hydrolysis) and is used for cleaning the surface of metals before soldering. Solder (see p. 641) "runs" on a hot brass, copper, or lead surface, *provided the latter is clean*, and adheres perfectly when cold. But it does not dissolve oxides, or melt them, and therefore cannot even reach the surface of the metal, much less adhere to it, if the slightest tarnish is present.

Zinc Oxide and Hydroxide and the Zincates. — The oxide ZnO is obtained as a white powder by burning zinc or by heating the precipitated basic carbonate. It turns yellow when heated, recovering its whiteness when cold. It is employed in making a paint — zinc-white or Chinese white — which is not darkened by hydrogen sulphide. It is used also as a filler in automobile tires.

The **hydroxide** Zn(OH)$_2$ appears as a white, flocculent solid when alkalies are added to solutions of zinc salts. It interacts as a basic hydroxide with acids, giving salts of zinc:

$$Zn(OH)_2 + H_2SO_4 \leftrightarrows ZnSO_4 + 2H_2O.$$
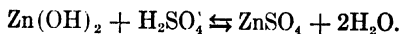
It also interacts with excess of the alkali employed to precipitate it, giving a soluble zincate, such as **potassium zincate** K$_2$ZnO$_2$:

$$H_2ZnO_2 + 2KOH \rightleftarrows K_2.ZnO_2 + 2H_2O.$$
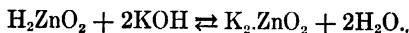
Zinc hydroxide is ionized **both as an acid and as a base:**

$$2H^+ + ZnO_2^= \rightleftarrows Zn(OH)_2 \text{ (dissolved)} \rightleftarrows Zn^{++} + 2OH^-$$
$$\text{\Updownarrow}$$
$$Zn(OH_2) \text{ (solid)}$$
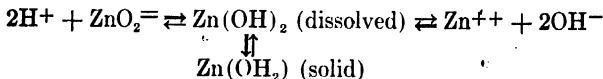
Substances which are both bases and acids are called **amphoteric.** The ionization of zinc hydroxide as an acid is less than that as a base, but both are small. Addition of an acid like sulphuric acid, however, furnishes hydrogen-ion; the hydroxyl ions combine with this to form water, and all the equilibria are displaced to the right. With a base, on the other hand, the hydrogen-ion is removed and the basic ionization simultaneously repressed, so that the equilibria are displaced to the left.

Zinc hydroxide interacts with ammonium hydroxide, giving the soluble **ammonio-zinc hydroxide** Zn(NH$_3$)$_4$.(OH)$_2$. In a solution of this substance, the zinc is existent almost entirely as part of a complex positive ion [Zn(NH$_3$)$_4$]$^{++}$. Consideration of this point will be deferred until Chapter XLIII, when it will be taken up in detail in connection with similar complex ions of copper.

Other Compounds. — **Zinc sulphate,** ZnSO$_4$,7H$_2$O, is made by the action of sulphuric acid on zinc or zinc oxide. It is used in preserving hides and as a mordant in cotton printing (see

dyeing, p. 591). Zinc sulphide ZnS (white) is precipitated practically completely when a solution of ammonium sulphide $(NH_4)_2S$ is added to a salt of zinc:

$$ZnSO_4 + (NH_4)_2S \rightarrow ZnS \downarrow + (NH_4)_2SO_4.$$
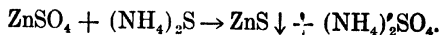
When hydrogen sulphide is employed instead

$$ZnSO_4 + H_2S \rightleftarrows ZnS + H_2SO_4$$
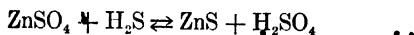
only a small part of the zinc is precipitated. The cause of this difference will come up for discussion in a subsequent section (p. 573). For the use of zinc sulphide as a paint ingredient (lithopone), see p. 508.

Analytical Reactions of Zinc Salts. — Zinc sulphide is precipitated by the addition of ammonium sulphide to solutions of zinc salts and of zincates. Sodium hydroxide gives the insoluble hydroxide, which, however, interacts with excess of the alkali, giving the soluble zincate of sodium. Compounds of zinc, when heated on charcoal with cobalt nitrate, give a zincate of cobalt, Rinmann's green $CoZnO_2$.

CADMIUM Cd

Aside from the rare mineral greenockite CdS, cadmium is found in small amounts (about 0.5 per cent), as carbonate and sulphide, in the corresponding ores of zinc. During the reduction, being more volatile than zinc, it distils over first (b.-p. 778°). The metal is white, and is more malleable than zinc. It displaces hydrogen from dilute acids (see p. 240). It is used in making fusible alloys.

Hydrogen sulphide precipitates the yellow sulphide CdS even from acid solutions of the salts. The substance is used as a pigment. The sulphide of cadmium, however, is less insoluble in water (see p. 328) than are the sulphides of copper and mercury, and is not completely precipitated from a strongly acid solution (e.g., HCl > 0.3N).

Analytical Reactions of Cadmium Compounds. — The cadmium ion Cd^{++} is bivalent and colorless. The yellow cadmium

sulphide is precipitated by hydrogen sulphide, even from acid solutions. The white, insoluble hydroxide is not soluble in sodium hydroxide, but interacts with ammonium hydroxide to form a soluble complex (compare zinc hydroxide, p. 564).

IONIC EQUILIBRIA

In view of the importance of ionic actions in the chemistry of the metals, we must now consider more closely the subject of ionic equilibria. The whole *basis* for this exact consideration *has already been supplied*, and only more specific application of the principles is demanded. The basis referred to, which should now be re-read, is contained in the discussion of chemical equilibrium in general (pp. 207-215). One important point may be briefly recapitulated here, as an aid to the reader.

Equilibrium in Reversible Reactions. — We saw (p. 211) that the point of equilibrium in the dissociation of phosphorus pentachloride:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2$$

is dependent upon the molecular concentrations of the reacting substances, and may be represented by the equation:

$$\frac{[PCl_3] \cdot [Cl_2]}{[PCl_5]} = K.$$

In this equation the quantities within the brackets represent the equilibrium concentrations of the respective substances, and K is the equilibrium constant of the reversible reaction. However much we may vary the molecular concentration of any one substance at any fixed temperature (say by adding excess of Cl_2 to the gaseous mixture), the only effect will be a re-adjustment of the equilibrium point such that the final ratio $[PCl_3] \cdot [Cl_2]/[PCl_5]$ is unchanged. In other words, the equilibrium constant K is a **fixed quantity.**

Application to Ionization. — Exactly the same principles can be applied to the ionic dissociation of an electrolyte. The be-

havior of acetic acid, a weak, slightly ionized acid, will serve as an illustration.

In normal solution (60 g. in 1 l.) acetic acid is only 0.004 ionized (p. 243), so that, in the equation for the equilibrium,

$$(0.996) \ HC_2H_3O_2 \leftrightarrows H^+ \ (0.004) + C_2H_3O_2^- \ (0.004),$$
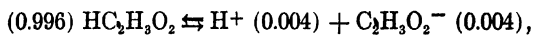
the relative proportions are as shown by the numbers in parentheses. If the whole of the acid (60 g.) were ionized, there would be 1 g. of hydrogen-ion per liter. Yet, even in the much smaller concentration actually present (0.004 g. per liter), the acid taste of the H^+ and its effect upon indicators can be distinctly recognized. If, now, solid *sodium acetate* is dissolved in the solution, the liquid *no longer gives an acid reaction* with one of the less delicate indicators, like methyl orange (see p. 263). The explanation is simple. Sodium acetate is highly ionized. It gives, therefore, a large concentration of acetate-ion to a liquid formerly containing very little. This causes a greatly increased union of the H^+ ions and $C_2H_3O_2^-$ ions to occur, and the former, being already very few in number, disappear almost entirely. Hence the solution becomes, to all intents and purposes, neutral. There is no less *acetic acid* present than before, but the concentration of hydrogen-ion is very much smaller.

Formulation and Quantitative Treatment of the Case of Excess of One Ion.—If $[H^+]$ and $[C_2H_3O_2^-]$ represent the *molecular concentrations* of hydrogen-ion and acetate-ion, respectively, and $[HC_2H_3O_2]$ that of the acetic acid molecules at equilibrium, then:

$$\frac{[H^+] \times [C_2H_3O_2^-]}{[HC_2H_3O_2]} = K.$$

The value of the *ionization constant* K is unchanged, whether the concentration of the solution of acetic acid is great or small, and even when another substance with a common ion is present. In the latter case, $[C_2H_3O_2^-]$ and $[H^+]$ stand for the *whole* concentrations of each of these ionic substances from *both* sources.

Now, in normal acetic acid $[H^+] = 0.004$, $[C_2H_3O_2^-] =$ 0.004 (for the number of each kind of ions is the same), and $[HC_2H_3O_2] = 0.996$, practically 1. Substituting in the formula:

$$\frac{0.004 \times 0.004}{1} = K \ (= 0.0_416).$$

When, however, sodium acetate is dissolved in the liquid until the solution is also normal in respect to this substance, which is 0.528 ionized in normal solution, the following additional equilibrium has to be considered:

$$(0.472) \ NaC_2H_3O_2 \rightleftarrows Na^+ \ (0.528) + C_2H_3O_2^- \ (0.528).$$
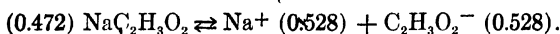
The concentration of acetate-ion from this source is 0.528, so that, in the mixture of acid and salt, the concentration of acetate-ion $[C_2H_3O_2^-]$ will be $0.528 + 0.004 = 0.532$, or 133 times larger than in the acid alone. Hence, in order that the ionization constant K may recover, as it must, its original value, $[H^+]$ must be diminished to something like $\frac{1}{133}$ of its former magnitude. That is, $[H^+]$ will become equal to about 0.00003,

$$\frac{0.00003 \times 0.532}{1} = K \ (= 0.0_416),$$

the rest of the hydrogen-ion uniting with a corresponding amount of the acetate-ion to form molecular acetic acid. The concentration of this increases only from 0.996 to 0.99997; in other words, so much is already present that its concentration is practically unchanged. The chief effect of adding this amount of sodium acetate therefore is, as we have seen, to reduce the concentration of the *hydrogen-ion* below the amount which can be detected by use of an indicator like methyl-orange.

This effect is of course reciprocal, and the ionization of the sodium acetate will be reduced also. But the acetate-ion furnished by the acetic acid is relatively so small in amount that the effect it produces on the ionization of the salt is imperceptible.

Although, therefore, acetate-ion and hydrogen-ion must disappear in equivalent quantities, for they unite, there is, however, so much of the former that the loss it sustains goes unremarked, while there is so little of the latter that almost none of it re-

mains. When substances of more nearly equal degrees of ioniza‑ tion are used, *both effects are relatively inconspicuous.* It is al‑ together impossible, for example, to reduce the concentration of the hydrogen-ion given by an *active* acid like hydrochloric acid, by addition of a salt containing a common ion, like sodium chloride, below the limit at which indicators are affected, for there is no way of introducing the enormous concentration of the other ion which the theory demands.

With more crude means of observation than indicators afford, effects like this last, however, may sometimes be rendered visible. This is the case with cupric bromide solution, to which potassium bromide is added (p. 253). The blue of the cupric-ion disap‑ pears from view, although much cupric-ion is still present, be‑ cause the brown color of the molecular cupric bromide covers it up completely. Another striking illustration is given on p. 209.

Special Case of Saturated Solutions. — The commonest as well as the most interesting application of the conceptions devel‑ oped above is met with in connection with saturated solutions, especially those of relatively insoluble substances.

The situation in a system consisting of the saturated solution and excess of the solute has been discussed already (read p. 156). In the case of potassium chlorate, for example, we have the fol‑ lowing scheme of equilibria:

$$KClO_3 \text{ (solid)} \rightleftarrows KClO_3 \text{ (dissolved)} \rightleftarrows K^+ + ClO_3^-$$
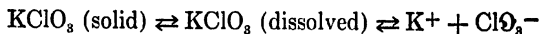
If we apply to the two reversible reactions represented in this scheme the principles which have been developed above, we obtain the two equations:

$$\frac{[KClO_3 \text{ (dissolved)}]}{[KClO_3 \text{ (solid)}]} = K_1 \tag{1}$$

$$\frac{[K^+] \cdot [ClO_3^-]}{[KClO_3 \text{ (dissolved)}]} = K_2 \tag{2}$$

where K_1 and K_2 are the equilibrium constants of the two reac‑ tions. By multiplying equation (1) by equation (2), we obtain a third relationship:

$$\frac{[K^+] \cdot [ClO_3^-]}{[KClO_3 \text{ (solid)}]} = K_1 . K_2 \tag{3}$$

Now $[\overset{\smile}{K}ClO_3$ (solid) $]$, the concentration of $KClO_3$ *in the solid state,* is invariable at any fixed temperature. Equation (3) consequently reduces to the form:

$[K^+] \cdot [ClO_3^-] = K_1 K_2 \cdot \lfloor KClO_3$ (solid) $\rfloor$ = a constant quantity.

In other words, **in a saturated solution, the product of the molar concentrations of the ions is a constant.** This product is called the **solubility product** of the substance. The **law of the constancy of the ion-product** in a saturated solution is one of the most useful of the principles of chemistry. It enables us to explain all the varied phenomena of precipitation and of the solution of precipitates in a consistent manner, as will be seen below. Upon the accuracy of the law of the constancy of the solubility product our whole system of quantitative analysis is based. It is of importance therefore to mention the fact that, although experimental test has shown that *both equation* (1) *and equation* (2), *by means of which the law was derived, are grossly inaccurate for all strong electrolytes* (neither K_1 nor K_2 remaining by any means constant as conditions are varied), yet *equation* (3), *the law itself, always approximates very closely to the truth.*

Illustration of the Principle of Solubility-Product Constancy. → When, to a **saturated** solution of one of the less soluble salts, a concentrated solution of a very soluble salt having **one ion in common** with the first salt is added, partial precipitation of the first salt is found to take place. This happens, for example, with a saturated solution of potassium chlorate, which is not very soluble (molar solubility 0.52, see Table). The concentrations $[K^+]$ and $[ClO_3^-]$ being small, one may easily increase the value for one of the ions, say $[ClO_3^-]$, fivefold, by adding a chlorate which is sufficiently soluble. To preserve the value of the product $[K^+] \times [ClO_3^-]$, the value of $[K^+]$ will then have to be diminished at once to one-fifth of its former value. This can occur only by union of the ionic material it represents with an equivalent amount of that for which $[ClO_3^-]$ stands. The molec-

ular material, so produced will thus tend at first to swell the value of [KClO₃]. But the value of [KClO₃] cannot be increased, for the solution is already saturated with molecules, so that the new supply of molecules, or others in equal numbers, will be precipitated. Hence the ionic part of the dissolved substance may be diminished, the equilibria (p. 569) may be partially reversed, and we may actually precipitate a part of the dissolved material without introducing any substance which, in the ordinary sense, can interact with it.

In point of fact, when, to a saturated solution of potassium chlorate, there is added a saturated solution of potassium chloride KCl (molar solubility, 3.9) or of sodium chlorate NaClO₃ (molar solubility, 6.4), a precipitate of potassium chlorate is thrown down.

Other Illustrations. — The precipitation of sodium chloride from a saturated solution, by the introduction of gaseous hydrogen chloride (p. 488), is to be explained in the same manner. The equilibria:

$$\text{NaCl (solid)} \rightleftarrows \text{NaCl (dissolved)} \rightleftarrows \text{Na}^+ + \text{Cl}^-$$
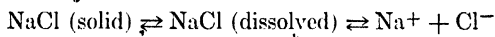
are reversed by the introduction of additional Cl^- from the very soluble, and highly ionized HCl.

The formation of potassium hydroxide (p. 480) ceases when a certain concentration has been reached. This occurs because the concentration of OH^-, which rapidly increases, is a factor in the solubility product of calcium hydroxide, $[\text{Ca}^{++}] \times [\text{OH}^-]^2$. With much OH^-, little Ca^{++} is required to give the constant numerical value of the product. When the concentration $[\text{Ca}^{++}]$ from the hydroxide has become about as small as that from the carbonate, the motive for the interaction has been removed. This principle is thus as important in industrial operations as it is in analytical and other laboratory experimentation.

Precipitation by Double Decomposition. — The mechanism of this type of reaction has already been discussed in some detail in an earlier chapter (p. 256), to which reference should here be made by the reader. The solubility-product law, however,

throws much additional light on the subject, and enables us to forecast the *completeness* of any given precipitation under given conditions.

The first thing to be remembered is that the precipitate which we observe, however insoluble its material may be, does not include *all* of the substance, but only the excess beyond what is required to saturate the water. **The liquid surrounding the precipitate is always a saturated solution of the substance precipitated.** If it were not so, some of the precipitate would dissolve until the liquid became saturated. Thus, for example, when we add ammonium sulphide solution to zinc chloride solution (p. 565).

$$(NH_4)_2S \rightleftarrows 2NH_4^+ + S^=$$
$$ZnCl_2 \rightleftarrows 2Cl^- + Zn^{++}$$
$$\Updownarrow \qquad \Updownarrow$$
$$2NH_4Cl \quad ZnS \rightleftarrows ZnS$$
$$\text{(dissolved)} \quad \text{(solid)}$$
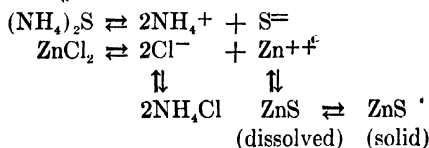
the liquid is a saturated solution of zinc sulphide, with the excess of this salt suspended in it as a precipitate.

Looking at the matter from this viewpoint, we perceive the application of the rule of solubility-product constancy. In this *saturated* solution the product of the ion-concentrations, $[Zn^{++}] \times [S^=]$, is constant. If the original solutions had been so very dilute that, when they were mixed, the product of the concentrations of these two ions had *not* reached the value of this constant, *no precipitation would have occurred.* As a matter of fact, the original salts are so extensively ionized in solution, and the solubility-product of zinc sulphide is so small, that in all ordinary mixtures the product $[Zn^{++}] \times [S^=]$ considerably exceeds the requisite value, and hence the salt is thrown down until the balance remaining gives the value in question. The **rule for precipitation,** then, is as follows: **Whenever the product of the concentrations of any two ions in a mixture exceeds the value of the ion-product in a saturated solution of the compound formed by their union, this compound will be precipitated.** Naturally the substances with small solubilities, and therefore small solubility-product constants, are the ones most frequently formed as precipitates.

Completeness of Precipitation. — In the above case, we precipitate zinc sulphide practically completely from solution by adding *excess* of ammonium sulphide. This substance, like all salts, is highly ionized in solution, and therefore a solution which contains it in excess contains a high concentration of sulphide ion $S^=$. The amount of zinc ion Zn^{++} that can exist simultaneously in such a solution is negligible, since otherwise the solubility-product of zinc sulphide would be exceeded., *Zinc is therefore precipitated quantitatively as zinc sulphide by addition of excess of ammonium sulphide to a solution of any zinc salt.* This is a fact which is turned to practical use in quantitative analysis.

If we attempt to carry out the precipitation with hydrogen sulphide instead of ammonium sulphide, however, we find that only partial precipitation of the zinc as sulphide occurs (p. 565). However great an excess of H_2S we add, precipitation is *incomplete*. The reason for this is immediately apparent from a study of the full ionic equations:

$$H_2S \rightleftarrows 2H^+ + S^=$$
$$ZnCl_2 \rightleftarrows 2Cl^- + Zn^{++}$$
$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$
$$2HCl \qquad ZnS \rightleftarrows ZnS$$
$$\text{(dissolved)} \quad \text{(solid)}$$
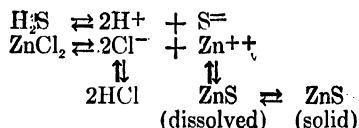
Hydrogen sulphide is so slightly ionized in solution that the concentration of sulphide ion $S^=$ that it supplies is extremely small. A large amount of zinc ion Zn^{++} can therefore remain in solution without the solubility-produce of zinc sulphide being exceeded.

Rule for Solution of Substances. — The **rule for solution of** *any* electrolyte follows at once from the foregoing considerations, and may be formulated by changing a few of the words in the rule just given: **Whenever the *product* of the concentrations of any two ions in a mixture *is less than* the value of the ion-product in a saturated solution of the compound formed by their union, this compound,** if present in the solid form, **will be** *dissolved.* When applied to the simplest case, this rule means

that a substance will dissolve in a liquid not yet saturated with it, but will not dissolve in a liquid already saturated with the same material. The main value of the rule lies, however, in its application to the less simple, but equally common cases, such as when an insoluble body is dissolved by interaction with another electrolyte.

Applications of the Rule: Solution of Insoluble Substances. — So long as a substance remains in pure water its solubility is fixed. Thus, with calcium hydroxide, the system comes to equilibrium at 18° when 0.17 g. per 100 c.c. of water (0.02 moles per liter) have gone into solution:

$$Ca(OH)_2 \text{ (solid)} \leftrightarrows Ca(OH)_2 \text{ (dissolved)} \leftrightarrows Ca^{++} + 2OH^-.$$
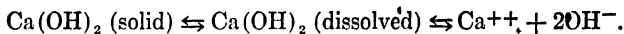
But if an additional reagent which can combine with either one of the ions is added, the concentration of this ion at once becomes less, the actual numerical value of the ion-product therefore begins to diminish, and further solution must take place to restore its value. Thus, if a little of an acid (giving H^+) be added to the solution of calcium hydroxide, the union of OH^- and H^+ to form water removes almost all the OH^- (see p. 259), and solution of the hydroxide proceeds until the acid is used up. There are now more Ca^{++} than OH^- ions present, but the *ion-product* reaches the same value as before, and then the change ceases. If a further supply of acid is added, the removal of OH^- to form H_2O begins again. Hence, with excess of acid, the calcium hydroxide finally all dissolves.

More specifically, if we assume that the calcium hydroxide is wholly dissociated in so dilute a solution (which is nearly true), each molecule forms one ion of Ca^{++} and two ions of OH^-. That is, each mole of $Ca(OH)_2$ gives one mole of Ca^{++} and two moles of OH^-. As the saturated solution contains 0.02 moles of the base, the molar concentration (assuming complete dissociation) of $[Ca^{++}]$ is 0.02 and of $[OH^-]$ is 0.04. Now, the ion-product is the product of the concentrations of all the ions formed, *i.e.* Ca^{++}, OH^-, and OH^-. The value of the product is therefore $[Ca^{++}] \times [OH^-] \times [OH^-]$ or $[Ca^{++}] \times [OH^-]^2$. That is, $0.02 \times 0.04^2 = 0.0_432$. Note that if the molecule gives two (or

three) ions of the same kind, the *whole* concentration of that ion is taken, and is also raised to the *second* (or third) *power*.

This particular action is a neutralization of an insoluble base. But the other kinds of actions by which, insoluble electrolytes pass into solution all resemble it closely, and differ only in details. The general outlines of the explanation are the same in every case. We proceed now to apply it to the common phenomenon of the solution of an insoluble salt by an acid.

Interaction of Insoluble Salts with Acids, Resulting in Solution of the Salt. — Zinc sulphide passes into solution when in contact with acids, especially active acids. Thus, with hydrochloric acid, it gives zinc chloride and hydrosulphuric acid, both of which are soluble:

$$ZnS + 2HCl \leftrightarrows ZnCl_2 + H_2S. \tag{1}$$
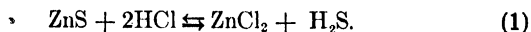
The action of acids upon insoluble salts is so frequently mentioned in chemistry and is so important a factor in analytical operations that it demands separate discussion. This example is a typical one and may be used as an illustration.

According to the rules already explained (p. 572), zinc sulphide (or any other salt) is precipitated when the numerical value of the product of the concentrations of the two requisite ions $[Zn^{++}] \times [S^=]$ exceeds the value of the ion-product for a saturated solution of zinc sulphide in pure water. When, on the contrary, the product of the concentrations of the two ions falls below the limiting value, a condition which may arise from the removal in some way either of the Zn^{++} or of the $S^=$ ions, the solid will dissolve to replace them until the ionic concentrations necessary for equilibrium with molecules have been restored or until the whole of the solid present is consumed. Here the sulphide-ion from the zinc sulphide combines with the hydrogen-ion of the acid (usually an active one) which has been added, and forms molecular H_2S:

$$S^= + 2H^+ \leftrightarrows H_2S. \tag{2}$$

It will be seen that the removal of the ions in this fashion can result in considerable solution of the salt only when the acid

produced is a feebly ionized one. Here, to be specific, the concentration of the S$^=$ in the hydrosulphuric acid equilibrium (2) above must be less than that of the same ion in a saturated zinc sulphide solution. Now hydrosulphuric acid belongs to the least active class of acids, and its pure solution contains only a very small concentration of S$^=$ (p. 323). There is, however, another factor in the situation which we have not yet taken into account. The hydrochloric acid which we used for dissolving the precipitate is a very highly ionized acid and gives an enormously greater concentration of hydrogen-ion than does hydrosulphuric acid. Hence the hydrogen-ion is in large excess in equation (2), and the condition for equilibrium, $\dfrac{[\mathrm{H}^+]^2 \times [\mathrm{S}^=]}{[\mathrm{H}_2\mathrm{S}]} = K$, will be satisfied by a correspondingly much smaller concentration of S$^=$. In this particular case, therefore, the [S$^=$] of the hydrosulphuric acid *is* far less than that given by the zinc sulphide. The whole change, evidently, depends for its accomplishment, not only on the mere presence of hydrogen-ion, but *on the repression of the ionization of the hydrosulphuric acid* by the great excess of hydrogen-ion furnished *by the active acid* that has been used. The complete scheme of the equilibria is as follows:

$$\mathrm{ZnS\ (solid)} \leftrightarrows \mathrm{ZnS\ (dissolved)} \leftrightarrows \mathrm{Zn}^{++} + \mathrm{S}^=$$
$$2\mathrm{HCl} \leftrightarrows 2\mathrm{Cl}^- + 2\mathrm{H}+$$
$$\qquad\qquad \updownarrow \qquad\quad \updownarrow$$
$$\qquad\qquad \mathrm{ZnCl}_2 \quad \mathrm{H}_2\mathrm{S} \rightleftarrows \mathrm{H}_2\mathrm{S}$$
$$\qquad\qquad\qquad\quad \text{(dissolved)} \quad \text{(gas)}$$
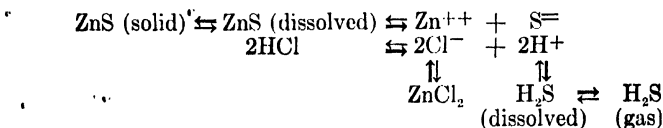
A generalization may be based on these considerations: **an insoluble salt of a given acid will in general interact and dissolve when treated with a solution containing another acid, provided that the latter acid is a much more highly ionized (more active) one than the former.**

Precipitates Insoluble in Acids. — But even active acids frequently fail to bring salts of weak acids into solution. Here the cause lies in the fact that such salts are even less soluble than those of the 'zinc sulphide type. Thus, even hydrochloric acid

(normal) will not appreciably dissolve cupric sulphide. The solubility product $[Cu^{++}] \times [S^=]$ for this salt is so small that, after an infinitesimal amount has gone into solution, the sulphide-ion concentration is sufficient, in spite of the repressive action of the large hydrogen-ion concentration furnished by the HCl, to bring the product $[Cu^+_+\!{}^+] \times [S^=]$ up to its maximum possible value. In this case the first link in the chain of equilibria:

$$\text{CuS (solid)} \leftrightarrows \text{CuS (dissolved)} \leftrightarrows Cu^{++} + S^= \quad\quad$$
$$2HCl \quad\quad \leftrightarrows 2Cl^- + 2H^+$$
$$\Updownarrow \quad\quad \Updownarrow$$
$$CuCl_2 \quad H_2S \rightleftarrows H_2S$$
$$\text{(dissolved)} \quad \text{(gas)}$$
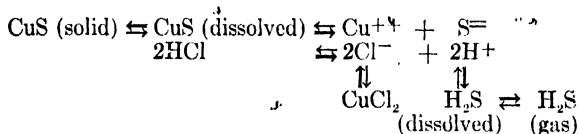
tends so decidedly backward that only the use of very concentrated acid will increase the concentration of the H^+ to an extent sufficient to secure even a slight advance of the whole action. We must add, therefore, to the above rule: **provided also that the salt is not one of extreme insolubility.**

Illustrations of the application of these generalizations are countless. Carbonic acid is made from marble (p. 422), hydrogen sulphide from ferrous sulphide (p. 327), hydrogen peroxide from sodium peroxide (p. 290), and phosphoric acid from calcium phosphate (p. 411). In each case the acid employed to decompose the salt is more active than the acid to be liberated. On the other hand, calcium phosphate is *insoluble* in acetic acid because this acid is weaker than is phosphoric acid. We have thus only to examine the list of acids showing their degrees of ionization (p. 244) in order to be able to tell which salts, if insoluble in water, will be dissolved by acids and, in general, what acids will be sufficiently active in each case for the purpose. In chemical analysis we discriminate between salts soluble in water, those soluble in acetic acid (the insoluble carbonates and some sulphides, FeS and MnS, for example), those requiring active mineral acids for their solution (calcium phosphate, zinc sulphide and the more insoluble sulphides, for example), and those insoluble in all acids (barium sulphate and other insoluble salts of active acids).

. **Precipitation of Insoluble Salts in Presence of Acids.** — The converse, of solution, namely, precipitation, depends upon the same conditions: an insoluble salt which is dissolved by a given acid cannot be formed by precipitation in the presence of this acid. Thus calcium phosphate or sulphide can be precipitated in presence of acetic acid, but not in presence of active mineral acids in ordinary concentrations. Cupric sulphide or barium sulphate can be precipitated in presence of any acid; but ferrous sulphide and calcium carbonate only in the absence of acids.

From this it does not follow that zinc sulphide, for example, cannot be precipitated if once an active acid has been added to the mixture. To secure precipitation, all that is necessary is to remove the excess of hydrogen-ion which is repressing the ionization of the hydrosulphuric acid. This can be done by adding a base, by adding ammonium sulphide, or even by adding sodium acetate.

Exercises. — 1. (a) How do the electrolytic methods of making calcium and magnesium differ? (b) Why not electrolyze an aqueous solution of magnesium chloride in making magnesium? (c) Why use both potassium and sodium chlorides in making magnesium? (d) Why is magnesium, but not potassium or sodium, liberated?

2. Why are magnesium and zinc not found free in nature?

3. Why does magnesium rust completely (in time), while zinc does not?

4. Make equations for: (a) the action of magnesium on hydrochloric acid; (b) the burning of magnesium in air; (c) the heating of magnesium carbonate; (d) the precipitation of magnesium hydroxide from the sulphate; (e) the hydrolysis of magnesium chloride.

5. Why is salt containing magnesium chloride, after mixing with sodium bicarbonate, no longer deliquescent?

6. What is the density of zinc vapor (air $= 1$)?

7. Make equations for: (a) the action of hydrogen sulphide on zinc oxide; (b) the precipitation of zinc hydroxide; (c) the action of sodium hydroxide on zinc hydroxide.

8. What will be the effect of adding a concentrated solution

of silver nitrate to a saturated solution of silver sulphate (see table of solubilities)?

9. Write full ionic equations for the reactions mentioned on p. 577.

10. Show, by means of ionic equations, why it is possible to prevent the precipitation of magnesium hydroxide when ammonium hydroxide is added to a soluble magnesium salt, by prior addition of ammonium chloride. (Use pp. 567-569.)

11. Why is it not possible, in the same way, to prevent the precipitation of magnesium hydroxide when sodium hydroxide is added to a soluble magnesium salt, by prior addition of sodium chloride?

CHAPTER XLI

ALUMINIUM AND THE RARE EARTH METALS

Thr family of trivalent elements to which the metal aluminium belongs includes the non-metal boron (p. 455), and several rare metals. On the right hand side of the fourth column of the periodic table we have **aluminium** (Al, at. wt. 27.0), **gallium** (Ga, at. wt. 70.1), **indium** (In, at. wt. 114.8), and **thallium** (Tl, at. wt. 204.0). On the left hand side there are **scandium** (Sc, at. wt. 45.1), **yttrium** (Yt, at. wt. 89.33) and **lanthanum** (La, at. wt. 139.0).

The Rare Elements of this Family. —Gallium and indium occur occasionally in zinc-blende, and were discovered by the use of the spectroscope. The former takes its name from the country (France) in which the discovery was made, and the latter from two blue lines shown by its spectrum.

Thallium is found in some specimens of pyrite and blende. It was discovered by Crookes, by means of the spectroscope, in the seleniferous deposit from the flues of a sulphuric acid factory. It received its name from the prominent green line in its spectrum (Greek, θαλλός, a green twig). It gives two complete series of compounds. In those in which it is trivalent (thallic salts), it resembles aluminium. Univalent thallium recalls both sodium and silver. Thallous hydroxide TlOH is soluble, and gives a strongly alkaline solution, but the chloride is insoluble in cold water. The solutions of the thallous salts are neutral. The metal is displaced from its salts by zinc.

Of the elements on the left side of the column, **scandium**, whose existence and properties were predicted by Mendelejeff (p. 362), is the best known. The metals of the **rare earths**, of which it is one, are found in rare minerals such as euxenite, gadolinite, orthite, and monazite, which occur in Sweden, Greenland, and the United States. The compounds of many of these

rare elements behave so much alike that separation is difficult: There are several with atomic weights near to that of lanthanum for which accommodation cannot easily be found in the periodic table (see p. 364). Ostwald has compared them to a group of minor planets such as in the solar system takes the place of one large planet.

ALUMINIUM

The Chemical Relations of the Element. — Aluminium is trivalent exclusively. Its hydroxide, like that of zinc (p. 564), is amphoteric, that is to say, it is feebly acidic as well as basic, and hence the metal forms two sets of compounds of the types $Na_3.AlO_3$ (sodium aluminate) and $Al_2.(SO_4)_3$. The salts of both series are more or less hydrolyzed by water, the former very conspicuously so.

Occurrence. — Aluminium is found very plentifully in combination, coming next to oxygen and silicon in this respect. The **felspars** (such as $KAlSi_3O_8$), the **micas** (such as $KAlSiO_4$), and **kaolin (clay)** $H_2Al_2(SiO_4)_2,H_2O$ are the commonest minerals containing it. Since the soil has been formed largely by the weathering of minerals like the felspars (see p. 525), clay and other products of the decomposition of such minerals constitute a large part of it. **Cryolite** is a double fluoride, $3NaF,AlF_3$: Various forms of the oxide and hydroxide are also found. **Bauxite** $(Al_2O_3,2H_2O)$ is a valuable hydrated oxide.

Manufacture and Physical Properties. — The making of aluminium on a large scale originated in C. M. Hall's discovery (**1886**) that the oxide could be electrolyzed in solution in molten cryolite. Iron boxes (Fig. 126), about 5 by 3 feet and 6 inches deep, are lined with a compressed mixture of coke and tar which is afterwards baked.

FIG. 126.

The lining forms the cathode, while the oxygen is liberated at the anodes — a series of rods of carbon about 3
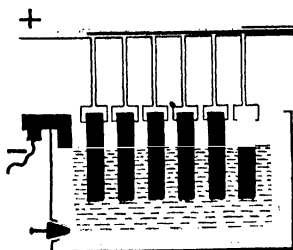
inches in diameter which are attached to copper rods. The cryolite is melted (1000°) by the arcs struck by the carbon rods. The latter are then raised somewhat, the aluminium oxide is added, and some coal (which floats) is thrown in to cover the surface and obscure the blinding glow. From time to time more of the oxide is added and the melted aluminium is tapped off. The oxide must be made from carefully purified bauxite, as the metal itself cannot be purified commercially. In 1866 it cost $250 to $750 per kilogram and now sells at about 50 cents. Forty years ago the whole world's production was only about 40 kilograms a year. In 1920 the United States alone consumed 90 million kilograms.

The metal melts at 659°, but is not mobile enough to make castings. It is exceedingly light (sp. gr. 2.6), and in tensile strength excels the other metals, with the exception of iron and copper. It is malleable, and the foil is taking the place of tin foil for wrapping foods. It has a silvery luster, and tarnishes very slightly, the *firmly adhering* film of oxide first formed protecting its surface. Although, comparing cross-sections, it is not so good a conductor of electricity as is copper, yet *weight for weight* it conducts better. It is difficult to work on the lathe or to polish, because it sticks to the tools, but the alloy with magnesium (about 2 per cent) called **magnalium** has admirable qualities in these respects. **Aluminium bronze** (5–12 per cent aluminium with copper) is easily fusible, has a magnificent golden luster, and possesses mechanical and chemical resistance exceeding that of any other bronze. The metal and its alloys are used for making cameras, opera-glasses, cooking utensils, the metal parts of dirigibles and aeroplanes, and other articles requiring lightness and strength, as well as for the transmission of electricity. The powdered metal, mixed with oil, is used in making a silvery paint.

Chemical Properties. — The metal displaces hydrogen from hydrochloric acid very easily. It liberates hydrogen also from boiling solutions of the alkalies, forming aluminates:

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2.$$
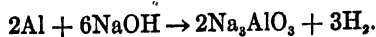
In consequence of its very great affinity for oxygen, aluminium displaces from their oxides the metals below it in the electromotive series. Thus, when a mixture of aluminium powder and ferric oxide (**thermite**) is placed in a crucible and ignited by means of a piece of burning magnesium ribbon, aluminium oxide and iron are formed:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe.$$
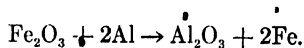
A temperature of 3000° to 3500° is produced by the action, the molten iron (m.-p. 1500°) collects at the bottom, and the molten aluminium oxide (m.-p. 2050°) floats to the top. This very simple method of making pure specimens of metals like chromium, uranium, and manganese, whose oxides are otherwise hard to reduce, is called by Goldschmidt, the inventor, **aluminothermy.** By preheating the ends of steel rails with a gasoline torch, firing a mass of thermite in a crucible above the joint, and allowing the iron to flow into the joint, perfect welds are made. In the same way, large castings, like propeller shafts, when broken, can be mended. The sulphides, such as pyrite, are reduced with like vigor by aluminium.

The largest part of the aluminium of commerce is used by steelmakers. When added in small amount (less than 1 : 1000) to molten steel, it combines with the gases, and gives sound ingots free from blow holes.

Aluminium Hydroxide Al(OH)₃. — The hydroxide is precipitated when ammonium hydroxide, or other alkaline hydroxide, is added to a solution of a salt of aluminium:

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 \downarrow + 3(NH_4)_2SO_4 \text{ (dslvd.)}.$$
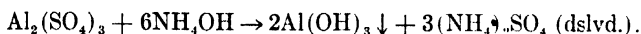
It tends to remain in colloidal suspension (p. 553), and forms a *white gelatinous precipitate.* It is *both weakly basic* and *feebly acidic* in chemical properties. In acids it dissolves forming salts of aluminium, such as the chloride $AlCl_3$ or sulphate $Al_2(SO_4)_3$. Solutions of these salts in water give an acid reaction, owing to hydrolysis (p. 469).

Aluminium hydroxide dissolves also in sodium hydroxide solution, to form **sodium aluminate** Na_3AlO_3:

$$3\text{NaOH} + \text{H}_3\text{AlO}_3 \rightarrow \text{Na}_3\text{AlO}_3 + 3\text{H}_2\text{O}.$$
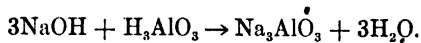
The aluminates are hydrolyzed by water, and their solutions have an *alkaline* reaction.

Aluminium hydroxide, precipitated from the sulphate, is used in sizing paper (to fill the capillaries and pores), in purifying water (see p. 585), and as a mordant (see p. 591) in dyeing. Delicate fabrics (cloth) are rendered waterproof by saturating them with aluminium acetate solution and boiling to promote the hydrolysis. The aluminium hydroxide is precipitated in the capillaries of the cotton or linen, rendering them non-absorbent.

Aluminium Oxide (Alumina) Al₂O₃. Al_2O_3. — **Corundum,** and the impure variety **emery,** are next to the diamond in the scale of hardness, and are used as abrasives. **Ruby** and **sapphire** are also crystallized aluminium oxide, containing traces of impurities (iron and titanium in the one case and chromium in the other) to which they owe their colors. By ingenious methods of fusing the oxide, "synthetic" sapphires to the extent of six million carats and rubies to the extent of ten million carats, are now made annually. The artificial gems are chemically identical with the natural ones, and can be distinguished only by the fact that they are free from microscopic bubbles and other defects. **Alundum,** an artificial abrasive, and refractory material for crucibles and muffles, is made by barely melting the oxide in the electric furnace.

Aluminium Sulphate Al₂(SO₄)₃,18H₂O. $\text{Al}_2(\text{SO}_4)_3, 18\text{H}_2\text{O}$. — The sulphate is manufactured by the action of sulphuric acid on bauxite. It crystallizes in leaflets, which usually have a faint yellow tinge due to the presence of iron ($\text{Fe}(\text{OH})_3$) derived from the mineral. The salt is used in fireproofing cloth, since, when heated, it melts in its water of hydration. It is also used as a source for pre-cipitated aluminium hydroxide in paper-making, water purification, and dyeing.

Alums. — When aluminium sulphate and potassium sulphate are dissolved together in equimolecular proportions, the solution deposits transparent octahedral (Fig. 44, p. 105) crystals of

hydrated potassium-aluminium sulphate $K_2SO_4,Al_2(SO_4)_3,24H_2O$. This salt is more easily freed from impurities (*e.g.*, compounds of iron) by recrystallization than is aluminium sulphate, and is therefore used instead of the latter in medicine, in dyeing (delicate shades), and to replace the cream of tartar (p. 544) in making baking powder.

Potassium-aluminium sulphate is a *double salt*, and is one of a large class known as **the alums**. The alums have the general formula $M_2{}^ISO_4,M_2{}^{III}(SO_4)_3,24H_2O$, and may be made as above by using a sulphate of a univalent metal with one of a trivalent metal. Thus, for M^I we may use K, NH_4, Rb, Cs, and Tl^I, and for M^{III}, Al, Fe^{III}, Cr^{III}, Mn^{III}, and Tl^{III}. All the alums crystallize in octahedra.

Sodium-alum, $Na_2SO_4,Al_2(SO_4)_3,24H_2O$, **ammonium-alum** $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$ and **chrome-alum** $K_2SO_4,Cr_2(SO_4)_3,$ $24H_2O$ are the most familiar alums after **potash-alum**. The first two are used as sources of aluminium hydroxide, and the last in the "fixing bath" to harden the gelatine on photographic films and plates.

Water Purification: Coagulation Process. — The suspended matter in water to be used for a domestic supply can be coagulated into larger particles by introducing a small amount of the gelatinous precipitate of aluminium hydroxide. These larger particles, which adsorb also the greater part of the bacteria, settle rapidly and the process therefore permits the use of relatively small settling ponds. Aluminium sulphate, made from crude bauxite, and lime are added to the water:

$$3Ca(OH)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(OH)_3.$$
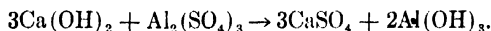
If the water has much temporary hardness, lime is not required:

$$3Ca(HCO_3)_2 + Al_2(SO_4)_3 \rightarrow 3CaSO_4 + 2Al(HCO_3)_3.$$
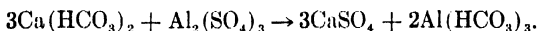
The carbonate of aluminium, being a salt of *both* a very weak acid and a very weak base, is extensively hydrolyzed (p. 470):

$$Al(HCO_3)_3 + 3H_2O \rightarrow Al(OH)_3 \downarrow + 3H_2CO_3$$
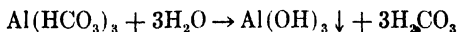
so that aluminium hydroxide is precipitated.

. Crude ferrous sulphate $FeSO_4$ (copperas), being in many places cheaper than aluminium sulphate, is often used instead of the latter. The lime precipitates ferrous hydroxide $Fe(OH)_2$. This is quickly oxidized to the red ferric hydroxide $Fe(OH)_3$, which coagulates the suspended matter.

Clay and Pottery. — By the action of water and carbon dioxide upon granite and other rocks containing felspar $KAlSi_3O_8$, the potash is slowly removed, and the compound is changed largely into a hydrated orthosilicate $H_2Al_2(SiO_4)_2,H_2O$. When pure, it forms **kaolin** or china clay, a white, crumbiy material. When washed away and redeposited, it usually acquires compounds of iron, the carbonates of calcium and magnesium, and sand (silica), becoming common clay. Ocher, umber, and sienna are clays colored with oxides of iron and manganese. Fuller's earth is a purer variety.

The plasticity of clay, a property connected with the colloidal nature of the kaolin, enables it to be fashioned into various shapes. When heated, it shrinks and becomes a hard, solid, porous mass, and does not melt. These two properties enable us to use it in making bricks, pottery, and porcelain. The presence of calcium and magnesium compounds makes the clay more fusible, because it permits the formation of fusible silicates of these metals. **Bricks** and **tiling** for roofs and drains are made of common clay and, when red, owe their color to oxide of iron Fe_2O_3. The firing is done with fuel gas in ovens or kilns of brickwork. To glaze drain pipes and some bricks, salt is thrown into the kiln. The water vapor, at a red heat, hydrolyzes the salt, hydrogen chloride is set free, and the sodium hydroxide gives with the clay a fusible sodium-aluminium silicate which fills the surface pores. Clay for fire brick (infusible) must contain silica, but no lime.

China and **porcelain** are made from pure clay, free from iron, to which a little of the more fusible felspar is added. After the first firing, the articles are porous (bisque), and must be covered with a glaze. A paste of finely ground felspar and silica, sometimes containing lead oxide, is spread on the surface, and the articles are fired again, at a higher temperature. Colored decora-

tions are added by means of suitable materials, mainly oxides of metals which give colored silicates. The third firing causes these oxides to interact and fuse with the glaze.

Ultramarine. — Pulverized *lapis lazuli*, a rare mineral of beautiful blue color, was used by artists in the past as a pigment. Gmelin (1828) found a way of making it artificially. A mixture of kaolin, sodium carbonate, sulphur, and charcoal is heated until a green mass is obtained. This mass is then pulverized and heated with more sulphur. The product is used as laundry blueing, in making blue-tinted paper, and with oil in making paint. It is also added in small amount to correct the natural yellow tint of linen, starch, sugar (p. 518), and paper-stock. By varying the mode of heating, without altering the composition, various colors from green to reddish violet can be obtained. No pure colored substance can be extracted from it. The variety of colors is due to different degrees of collodial dispersion of some substance suspended in the solid (compare p. 592).

Cement. — *Portland cement* is made by heating a pulverized mixture of a material rich in lime, such as limestone $CaCO_3$, with one in which silica, iron oxide and alumina are the main constituents, such as common clay. Some natural rocks contain all of the necessary elements in suitable proportions. The finely powdered material is first *burnt* or raised to a temperature of 1400–1600°, at which temperature it fuses partially and forms lumps or *clinkers*. When these have cooled, they are mixed with 2–3 per cent of gypsum and pulverized again. The resulting product is Portland cement, the manufacture of which in the United States alone now exceeds 100,000,000 barrels (of 380 pounds) yearly.

Portland cement is essentially a mixture of calcium silicate and calcium aluminate, with excess lime. The calcium silicate is simply a filler. The calcium aluminate is hydrolyzed on addition of water, according to the equation:

$$Ca_3(AlO_3)_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2H_3AlO_3.$$
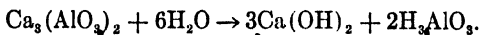
The calcium hydroxide thus formed slowly crystallizes, connect-

ing the particles of the calcium silicate. The aluminium hydroxide fills the interstices and renders the whole compact and impervious.

The small amount of *gypsum* added regulates the setting time of the cement. The *iron oxide* is necessary to assist in the burning and to lower the temperature at which the mixture begins to fuse. If too small a quantity of *excess lime* is present, the cement will be unsound and crack on drying. Too little excess lime gives a cement which sets too quickly and is lacking in strength.

Concrete is a mixture of cement with sand and crushed stone or gravel, all made into a paste with water. It sets to a solid mass, suitable for walks, and for the foundations, walls, and floors of buildings. Since no carbon dioxide from the air is required in the hardening process (contrast with p. 500), it sets equally well under water (hence hydraulic cement), and is employed in constructing dams, levees, and the foundations of bridges. Reinforced concrete contains twisted rods of iron, embedded in the mass, and is much used in building construction.

Blast-furnace slag, when pulverized and heated with limestone, has been found to yield an excellent quality of cement, and a valuable use has thus been found for what was formerly an annoying encumbrance.

Analytical Reactions of Aluminium Compounds. — The alkalies, and alkaline solutions like that of ammonium sulphide, precipitate the white hydroxide. The product is soluble in excess of the active alkalies. Soluble carbonates also throw down the hydroxide. Aluminium compounds, when heated strongly in the flame with cobalt salts, give a blue aluminate of cobalt $Co(AlO_2)_2$.

Exercises. — 1. What are the differences between zinc and aluminium, and their corresponding compounds?

2. Construct equations showing, (a) the hydrolysis of aluminium sulphate (p. 469), (b) the interaction of aluminium sulphate and cobalt nitrate in the Bunsen flame.

3. Formulate the ionization of aluminium hydroxide (compare p. 564).

4. Why does zinc hydroxide, in spite of its feebleness as an

acid, dissolve in ammonium hydroxide, while aluminium hydroxide does not (see p. 564)?

5. Make equations for the following actions: (a) aluminium on hydrochloric acid; (b) aluminium on mercuric chloride $HgCl_2$; (c) displacement of manganese from manganese dioxide by aluminium.

6. Why is the tarnish on aluminium the oxide, and not the carbonate (as on Zn and Mg)? What qualities in a tarnish enable it to protect the metal from further oxidation (p. 582)?

7. Make equations for the action of bicarbonate of soda on aluminium sulphate (alum baking powder) when heated. Explain what raises the bread.

8. Why does ammonium sulphide precipitate aluminium hydroxide, and not aluminium sulphide, from solutions of soluble aluminium salts?

SYNTHETIC ORGANIC PRODUCTS

MENTION was made several times in the preceding chapter of the use of salts of aluminium in dyeing. A brief summary of the chemistry of dyeing and dyestuffs is all that can be presented here. A still more restricted résumé of some other important synthetic organic products is also given. The products included are, on the *constructive* side, **perfumes, drugs** and **plastics** (including **rubber**); on the *destructive* side, **explosives** and **toxic gases.**

Some dyes, perfumes and drugs are still, of course, obtained from natural sources, and synthetic rubber continues to show but little promise of superseding plantation rubber in the near future. Nevertheless, the interest of the chemist in the fields here under discussion is almost entirely *synthetic*, seeking to duplicate natural products by laboratory methods and to discover new products of even greater use to humanity.

Dyeing. — The problem of the dyer is to confer the desired color upon a fabric made, usually, of cotton, linen, wool, or silk, and to do this in such a way that the dye is *fast* to (*i.e.*, is not removed or destroyed by) rubbing and light, and often, also, to washing with soap. To understand the means by which this is achieved, it must be noted that cotton and linen consist of smooth hollow fibers (A, Fig. 127) of cellulose Wool (B) is made of hollow fibers with a scaley surface, and silk of solid filaments, but both these substances are composed of proteins (pp. 511, 531). Now, the proteins are much more active chemically than is cellulose, and also, as colloidal materials, seem to have a much greater tendency to adsorb other substances (compare p. 556) than has cellulose. Hence, accidental stains on wool or silk are much less often removable than are those on cotton, and when samples of the three materials are dipped in a solution of

a dye, the first two are permanently dyed, while from the last most dyes can be completely washed out with water.

Three modes of dyeing may be mentioned:

1. **Insoluble Dyes.** If the colored body can be produced by precipitation, after the solution has filled the capillary and wall of every fiber of the goods, then, if the dye is sufficiently insoluble, it is mechanically, imprisoned in every fiber and cannot be washed out. This plan may be applied to any kind of goods. For example, if cotton, silk, or wool is first boiled in a solution of lead acetate, and is then soaked in a boiling solution of potassium chromate K_2CrO_4, it is dyed a brilliant, permanent yellow. Lead chromate is the colored body:
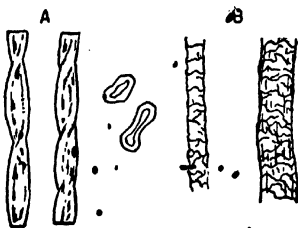
$$Pb(CO_2CH_3) + K_2CrO_4 \leftrightarrows 2K(CO_2CH_3) + PbCrO_4 \downarrow.$$
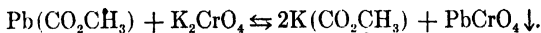
The part precipitated on the outside of the goods can be, and is, at once washed off by rubbing in water, but the particles inside the fibers can come out only by being dissolved, and they are insoluble in water. **Indigo** $C_{16}H_{10}N_2O_2$, which is used in larger amounts than any other dye, belongs to this class. The cloth is saturated with an alkaline solution of indigo white $C_{16}H_{12}N_2O_2$, a soluble, slightly acid substance, and the oxygen of the air subsequently oxidizes this and deposits the insoluble indigo blue within the fibers:

$$2C_{16}H_{12}N_2O_2 + O_2 \rightarrow 2C_{16}H_{10}N_2O_2 \downarrow + 2H_2O.$$
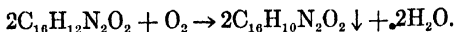
2. **Mordant or Adjective Dyes.** Since cotton is inactive chemically and has but a slight tendency to adsorb dyes, it is usually necessary first to introduce into the fibers of cotton some colloidal substance with greater adsorptive powers. Substances of this kind are *tannic acid* (p. 706) for basic dyes, and *gelatinous colloidal hydroxides*, such as those of aluminium, tin, iron and chromium, for non-basic (including acid) dyes. They are called **mordants** (Latin, mordere, *to bite*). Thus, if in three jars we place

very dilute solutions of aluminium sulphate, ferric chloride $FeCl_3$ and chromous acetate $Cr(CO_2CH_3)_2$, then add a few drops of a solution of a dye to each, and finally introduce a little of a base (like sodium hydroxide) to precipitate the hydroxide of the metal, this hydroxide will adsorb the dye and carry it into the precipitate. Such a precipitate of mordant and dye, is called a lake. With the same dye, the three lakes have different colors. Thus, in the above-mentioned experiment, if a'izarin (madder) is used as the dye, the colors are red (Turkey red), violet, and maroon, respectively. This is probably due to the different degrees of dispersion in the three colloidal materials. If aluminium hydroxide is to be used, by first saturating the cloth with hot aluminium acetate solution (p. 584), or by using first aluminium sulphate and then ammonium hydroxide, the aluminium hydroxide is precipitated within the fibers of the goods. When the material is then dyed, the coloring matter is adsorbed by the mordant, with which it forms an insoluble lake, within the fibers. Basic dyes, like *Malachite green* and *Methylene blue*, behave similarly with tannic acid, or an insoluble salt of tannic acid, as mordant. It will be seen that, so far as the fabric is concerned, this process, like the first, is a mechanical one, and is independent of the chemical nature of the goods.

3. **Direct or Substantive Dyes.** Most organic dyes are direct dyes on silk or wool, and require no mordant with these materials. The actions seem to be sometimes chemical, but more often cases of adsorption by the silk or wool (both colloids) themselves. A few dyes are also fast on cotton. *Congo-red* is fast both on cotton and wool, but is no longer much used. *Chrysophenin* is now one of the commonest dyes of this class. These dyes, which are sodium salts of complex organic acids, are *colloids* like soap (p. 554), and are salted out within the fibers of the goods by adding sodium sulphate to coagulate them and assist the adsorption by the cotton. Once adsorbed in this way, unlike soap, they cannot be washed out.

Dye-stuffs. — Natural dye-stuffs have now been almost entirely superseded by manufactured products, which can be prepared more cheaply and are of superior quality. *Logwood*,

still used as a black mordant dye for silk, is the only important, exception. The total value of natural dyes imported into the United States in 1919 was only $1,250,000, while the artificial dyes made in the country in the same year were worth over $70,000,000.

The vast bulk of synthetic dyes are built up from ring hydrocarbons (p. 440) and their derivatives, extracted from coal tar (p. 538). By substituting suitable groups into the molecule of the simpler *colorless* products, more complex derivatives with great brilliancy of color are obtained. Thus indigo, formerly the most extensively used of all natural dyes, is now manufactured most conveniently with aniline (p. 441) as a starting-point. Alizarin (Turkey red), once extracted from *madder root,* is obtained from *anthracene.*

By varying the position of the substituted groups in the molecule, the most delicate variations in color can be effected. The most precious of all dyes in ancient times was *Tyrian purple,* obtained from certain species of sea snails (Murex). The secret of preparing this substance was lost for centuries, but in 1909 Friedlaender gathered 12,000 of these mollusks and succeeded in isolating 1.5 grammes of the coloring material for analysis. He showed it to be a *derivative of indigo,* containing two bromine atoms in place of two of the hydrogens. This identical substance had been prepared synthetically five years earlier, but found to be *inferior* to another dye containing the bromine atoms in different positions in the molecule!

Perfumes. — Many natural perfumes and fruit flavors can also be produced synthetically. The basis of most of these consists of **esters** (p. 437). The fragrance of ripe *apples* is due to minute amounts of the amyl esters of formic, acetic and caproic acids. In *bananas* the characteristic ester is amyl acetate; in *grapes* it is methyl anthranilate. *Almond* flavor is due to benzaldehyde, $C_6H_5.CHO$; the smell of *geraniums* to diphenyl ether, $(C_6H_5)_2O$. The chief ingredient of *otto of roses* is geraniol; of the *vanilla* bean, vanillin; of the perfume sold as *"new mown hay,"* coumarin; all complex hydrocarbon derivatives which are now commercial products. Some of the synthetic flavors

and perfumes on the market are identical with the substances that give odor to fruits and flowers; others are merely more or less adequate imitations. Thus, natural *oil of wintergreen* is essentially the same as synthetic methyl salicylate. On the other hand amyl valerate, which is sold as apple essence, is not contained in the fruit, though it smells like it. Most perfumery nowadays, including the most expensive, consists of mixtures of natural and synthetic products.

Drugs. — In the same way, many drugs formerly obtained from natural sources are now built up in the laboratory, and many new compounds have been made which possess as valuable medicinal properties as any found in nature. The first stage in this work consisted in determining the constitution of the active ingredients of plant products. *Quinine* was isolated from cinchona bark, *morphine* from the seed capsules of the opium poppy, *strychnine* from the seeds of *nux vomica*. These and other substances of similar character are now classed together as **alkaloids**, complex nitrogenous substances possessing basic properties. The structure of many of the alkaloids is now completely worked out. It is not necessary, however, to construct the entire complicated molecule if the same results can be secured with simpler substances, and this has been demonstrated already in many instances.

Aspirin is an ester of salicylic acid $C_6H_4.OH.COOH$; *acetanilide* is a derivative of aniline $C_6H_5.NH_2$. Acetophenone (*hypnone*), $C_6H_5.CO.CH_3$, is used as a hypnotic. *Novocaine*, prepared from diethylaniline, has practically replaced the natural alkaloid *cocaine* in dentistry. *Saccharin* is obtained from toluene; its solution in water has an intensely sweet taste, hence it is used as a substitute for sugar in war times and in cases of diabetes. It has no food value, however, and hence cannot replace sugar in nutrition.

Plastics. — These are substances, like celluloid, which can be moulded or shaped into any desired form. Among natural plastics may be mentioned resins, gums, and rubber. Synthetic rubber equal to the natural product in durability and cheapness

has still to be prepared (see p. 488), but many other plastics are now of considerable industrial importance.

Certain *cellulose* plastics have already been described (p. 515). Cellulose behaves chemically like an *alcohol*, and as such forms *esters* with acids (see p. 437). When cotton is treated with acetic acid (in the form of acetic anhydride $(CH_3.CO)_2O$, see p. 311) it gives cellulose acetate. The viscous liquid dries to a tenacious film. On account of its waterproof character, non-inflammability and non-conductance of electricity, it is now used for coating the wings of aeroplanes, for making moving-picture films, and for insulating electric wires. Artificial horse-hair (*e.g.*, for making women's hats) and bristles for hair brushes are made of it.

By the action of nitric acid upon cellulose, various *cellulose nitrates* may be formed, according to the number of OH groups replaced by NO_3 (see guncotton, below). An incompletely nitrated ester, when worked between rollers with camphor* and a little alcohol, forms a viscous solution. When the alcohol evaporates, a transparent colorless solid, celluloid, remains. Photographic films are made by rolling the dough into sheets. Fillers and dyes can be added to the dough and the latter can be moulded to any form. In this way ivory-like or black combs and brush handles, opaque white knife handles, articles of "artificial amber" and so forth can be made.

The same sort of guncotton dissolves in a mixture of alcohol and ether, giving a solution called collodion, used in photography and in medicine.

When collodion is forced under great pressure through minute holes in a steel die, the threads dry as they issue from the openings and can be wound on spools. The product is treated with an alkali, which decomposes the ester, leaving a material of the composition of the original cotton. The product is another form of artificial silk (p. 515).

Another plastic, not chemically related to the preceding, is bakelite, prepared from formaldehyde CH_2O and phenol C_6H_5OH

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* A white solid with the formula $C_{10}H_{16}O$, obtained commercially by dis-tilling with steam the wood of the camphor tree, but recently also prepared synthetically.

(carbolic acid). Under suitable heat treatment the mixture grad-
ually sets to a solid, hard, infusible, resinous mass, which is insol-
uble in all common solvents. Before it sets, it can be dyed or
"filled," and it can be applied as lacquer, or moulded to any form
Switchboards, dolls, ornamental buttons, artificial jewels, phono-
graph records, billiard balls, and stereotyping matrices are
amongst the objects into which it is now fashioned.

Explosives. Nitroglycerine. — Some inorganic explosives,
gunpowder (p. 481) and ammonium nitrate (p. 401), have been
discussed in earlier chapters. The main organic explosives are
also compounds of nitrogen.

As already mentioned, the alcohols interact with inorganic
acids, as well as with organic ones, to produce esters. A familiar
illustration is met with in the manufacture of nitroglycerine
(glyceryl trinitrate) by the action of glycerine and nitric acid:

$$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(NO_3)_3 + 3H_2O.$$
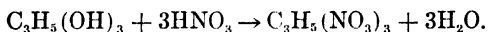
To assist in the liberation of the water, the nitric acid is mixed
with a dehydrating agent. The glycerine then is added slowly
to the cooled reagents. The nitroglycerine is an almost *color-
less oil* which floats to the surface of the acid mixture. It is
shaken repeatedly with water, in which it is insoluble, and then
with sodium carbonate solution, in order to free it from all traces
of the acids.

Nitroglycerine *explodes* violently, often from the slightest
shock. It owes this power to the fact that its carbon and hydro-
gen can combine with the oxygen it contains to form carbon
dioxide and water:

$$2C_3H_5(NO_3)_3 \rightarrow 6CO_2 + 5H_2O + 3N_2(+ O).$$
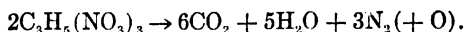
The latter are very stable substances and much heat is liberated
in forming them. They are both produced as gases and, at the
high temperature of the action, they and the nitrogen tend to
occupy a great volume — or to exert an enormous pressure in the
effort to do so (compare p. 401).

The explosion is also so *sudden*, compared with that of gun-
powder, that nitroglycerine would shatter the breech of a rifle

before the bullet had time to move. It also pulverizes rock, instead of breaking it into fragments of usable size. • For these reasons, as well as on account of the danger in handling, and impossibility of safely transporting the substance, it is made into blasting gelatine (see p. 598). The old form of dynamite was made by soaking a porous earth with nitroglycerine.

Guncotton. — When cotton is steeped for half an hour in a cooled mixture of nitric and sulphuric acids, it is converted into cellulose trinitrate or **guncotton**:

$$C_6H_7O_2(OH)_3 + 3HNO_3 \rightarrow C_6H_7O_2(NO_3)_3 + 3H_2O.$$
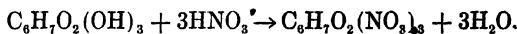
The equation, as written above, shows that three hydroxyl groups OH in the empirical cellulose formula $C_6H_{10}O_5$ are replaced by three nitrato groups NO_3, with simultaneous formation of three molecules of water. The sulphuric acid hastens the reaction and carries it to completion by acting as a dehydrating agent (see p. 345). The fibers have the same appearance as before, but are crisper to the touch. The guncotton is washed thoroughly with water to remove the acids, which would cause slow decomposition and perhaps accidental explosion. •

Dried guncotton burns briskly (deflagrates) when set on fire. While wet, it can be moulded and cut without danger. It explodes only when "set off" by a small amount of another explosive. Fulminate of mercury $Hg(ONC)_2$, used in percussion caps, is commonly employed. By such means the explosion is brought about in wet guncotton as easily as in dry.

In pure form guncotton is used only in torpedoes and submarine mines. It explodes too rapidly to be used in fire-arms or for blasting.

Smokeless Powder and Dynamite. — The violence of guncotton is reduced by compressing it, and still more by dissolving it and allowing the solvent to evaporate. Thus, cordite is made by dissolving guncotton (65 parts), nitroglycerine (30 parts) and vaseline (5 parts) in acetone. The resulting paste is rolled and cut into pieces of different dimensions, according to the rate of explosion desired. When the acetone evaporates, the horny

córdite remains. These explosives are *smokeless* because they differ from gunpowder (p. 482) in yielding no solids when they decompose.

Blasting gelatine, giant powder, and other forms of **dynamite** are made by dissolving guncotton in nitroglycerine. Substances like nitrate of sodium or of ammonium and sawdust or flour are added to adjust the rate of explosion so that, for example, coal may be split up, but not shattered.

High Explosives. — These are substances which develop their explosive effect at an extremely rapid rate, and are used therefore when a shattering effect of great violence is required, for example in *bursting shells* or in *anti-submarine mines*. **Trinitrotoluene** (TNT) is made by nitrating *toluene* (p. 440), **picric acid** (trinitrophenol) by nitrating *phenol*. Picric acid* is a strong acid and forms salts which, with the exception of ammonium picrate, are more sensitive to shock and friction than the acid itself. The action of this explosive on the metals with which it comes in contact must therefore be guarded against. TNT, however, is inert towards metals, and is insensitive towards ordinary shocks. It melts at a low temperature (80°), and so can be readily liquefied and poured into shells. Mixed with ammonium **nitrate**, it gives **amatol** (p. 382).

Toxic Gases. — The poisonous substances employed in the Great War were mainly synthetic organic products. Most of these, it is true, were not gases, but liquids or solids of low volatility. Their vaporization was, however, favored by the explosion of the shell in which they were contained, part of the material being converted to gas by the heat of the explosion and the remainder being scattered around in a finely divided condition. Some of the substances used were so powerful in their action upon the human system that a concentration of 1 part in 10,000,000 in the air was sufficient to incapacitate anyone unprotected with a gas-mask.

* Picric acid is an interesting example of the close interrelation of synthetic organic compounds. It is used in dyeing to give a yellow color, in warfare as an explosive and in medicine as an antiseptic. It may happen that picric acid is used in a base hospital to cure the wound that picric acid caused.

The first method employed in gas warfare was to release a highly volatile poisonous substance (*chlorine*, or a mixture of chlorine and *phosgene* $COCl_2$) from cylinders under pressure. A cloud of gas was thus evolved, which under favorable wind conditions was carried over the enemy's lines. This *cloud method* was soon abandoned in favor of the *shell* method described above. Among the substances thus employed may be mentioned *chlorpicrin* $CCl_3.NO_2$ (made by the action of bleaching powder and lime upon picric acid) and *mustard gas* $(CH_2Cl.CH_2)_2S$. The latter substance, the chemical name of which is dichlordiethyl sulphide, may be regarded as diethylether (p. 436) in which oxygen is replaced by sulphur and two hydrogen atoms are replaced by chlorine. It was produced by the action of ethylene C_2H_4 upon sulphur monochloride S_2Cl_2.

Both of the above substances are actually toxic, that is, a sufficient concentration will induce death. Many other substances were used, however, which merely put the victim temporarily out of action. Among these were *lachrymatories* (tear-producing substances) such as benzyl bromide $C_6H_5.CH_2Br$, and *sternutatories* (sneeze-producing substances) such as diphenylchlorarsine $(C_6H_5)_2AsCl$. The latter substance is a derivative of arsine AsH_3 (p. 665), the three hydrogen atoms being replaced by two phenyl groups C_6H_5 and one chlorine. Mustard gas in very low concentration also acted as a skin irritant.

The methods employed for obtaining protection against toxic gases have already been discussed (p. 536).

Exercises. — 1. Write graphic formulæ (see Chapter **XXX**) for the following synthetic essences: ethyl formate, ethyl butyrate, benzaldehyde, diphenyl ether.

2. What chemical change would occur after mixing nitroglycerine with sodium hydroxide solution? Name the kind of reaction and give the equation.

3. When nitroglycerine explodes, in what relative volumes are steam, carbon dioxide, and nitrogen produced? What principle is used in answering this question?

4. Make an equation for the decomposition of guncotton similar to that given for nitroglycerine (p. 596).

5. Make an equation for the denitration of guncotton by an alkali.

6. Write the graphic formulæ for the following substances: acetic anhydride, trinitrotoluene, picric acid, phosgene, chlorpicrin, mustard gas, benzyl bromide, diphenylchlorarsine.

CHAPTER XLIII ·

COPPER AND MERCURY

Up to the present we have followed fairly closely, in our order of presentation of the metals, the electromotive series on p. 240. If we were to continue on this basis, the next two elements to come up for consideration would be manganese and chromium. The chemical relations of these elements, however, are so complex that it is advisable to postpone their discussion until a later chapter. We shall consequently resume our study of the metals by taking up at this point two elements which will introduce us to these complexities of behavior somewhat more easily — namely copper and mercury.

Although these metals are placed in different columns of the periodic system, they offer many striking resemblances, as will appear in the following sections. Both elements fall below hydrogen in the electromotive series.

• COPPER Cu

Chemical Relations of the Element. — Copper (Cu; at. wt. 63.57) is the first metallic element showing two valences which we have encountered. In such cases two more or less complete, independent series of salts are known. These are here distinguished as **cuprous** (univalent) and **cupric** (bivalent) salts.

The chief cuprous compounds are Cu_2O, $CuCl$, $CuBr$, CuI, $CuCN$, Cu_2S. The cuprous compound is in each of these cases more stable (p. 43) than the corresponding cupric compound, and is formed from the latter either by spontaneous decomposition, as in the cases of the iodide and cyanide $(2CuI_2 \rightarrow 2CuI + I_2)$, or on heating. The cuprous halides and cyanide are colorless and insoluble in water.

The cupric compounds are more numerous, as they include also salts of oxygen acids, like $CuSO_4$, $Cu(NO_3)_2$, etc. The anhydrous

salts are usually colorless or yellow, but cupric-ion Cu^{++} is blue, and so, therefore, are the aqueous solutions of the salts. The cupric are more familiar than the cuprous compounds, since cupric oxide, sulphate, and acetate are the compounds of copper which most frequently find employment in chemistry and in the arts. All the soluble salts of copper are poisonous.

In addition to (1) having **two valences** Cu^I and Cu^{II}, and therefore two series of compounds (*two* oxides, *two* chlorides, etc.), *each* of these states of copper also joins with other elements to form (2) **complex positive ions** such as $Cu(NH_3)_2^+$ and $Cu(NH_3)_4^{++}$, just as hydrogen and ammonia form the complex positive ion NH_4^+, and the univalent form also gives (3) stable **complex negative ions** such as $Cu(CN)_2^-$, $CuCl_2^-$. Only zinc and cadmium, among all of the metallic elements discussed in the preceding chapters, showed any of these peculiarities. Many of the metals to be discussed later exhibit one or more of them, however. **Especial attention should therefore be given to the chemistry of copper,** in order that the behavior which such relations entail may be mastered, and the same relations may be instantly recognized and understood when they reappear in other connections.

Occurrence. — Copper occurs *free* in considerable amounts, particularly on the Michigan shore of Lake Superior. **Cuprous oxide** Cu_2O and basic carbonates, like **malachite** $CuCO_3,Cu(OH)_2$, are less common. The latter is often used as an ornamental stone. A large proportion of commercial copper is obtained from **chalcopyrite** Cu_2S,Fe_2S_3.

Metallurgy. — The free copper, after being concentrated (freed from gangue) by washing, is smelted with a flux. The carbonate is roasted, leaving the oxide. The oxides are reduced with coal.

The sulphide ores are more difficult to reduce, and the presence of so much iron complicates the process. They are *first* roasted. This removes much of the sulphur as sulphur dioxide, leaving Cu_2O and Fe_2O_3. *Next* the roasted material is treated in a blast furnace (p. 693), along with "green" (unroasted) ore,

sand (if silica is not present in the ore), and coke. Some of the
iron is oxidized and removed in the slag (as silicate). The prod-
uct, known as copper "matte," is a mixture of cuprous sulphide
Cu_2S with ferrous sulphide FeS. The *third* stage is to bessemer-
ize (see p. 696) the melted matte with sand in a converter. Here
the rest of the iron is oxidized and eliminated as silicate in the
slag, and the sulphur escapes as SO_2. The slag and metallic
copper are poured separately. The latter gives off some dis-
solved sulphur dioxide in bubbles as it solidifies and, from its ap-
pearance, is named **blister copper**. *Finally,* since the copper
now contains dissolved cuprous oxide Cu_2O, the blister copper
is melted and "poled," by stirring with green wood. The gases
(hydrocarbons, etc., p. 535) given off by the heated wood reduce
the oxide to copper. If the copper is to be refined electro-
lytically (p. 613), it is then cast in plates 3 feet square and
¾ inch thick.

The old methods of concentrating copper sulphide ores by
simple washing left large amounts of copper in the rejected
gangue. Recent **flotation processes** prevent this loss. The ore
is finely ground and beaten up with water containing a small
quantity of oil. The particles of copper sulphide become wetted
by the oil, the particles of gangue are preferentially wetted by
the water. When air is forced through the pulp, the copper sul-
phide particles float with the froth to the top and are scraped off,
while the gangue sinks to the bottom. Sixty million tons of
poor grade ore per year are now treated by this method.

Physical and Chemical Properties. — Copper is red by re-
flected and greenish by transmitted light. It melts at 1083°. Its
specific gravity is 8.93.

In ordinary air copper becomes slowly covered with a green
basic carbonate (*not* verdigris, p. 611). It does not decompose
water at any temperature or displace hydrogen from dilute acids
(p. 64). The metal attacks oxygen acids (pp. 333, 397), how-
ever. Sea-water and air slowly corrode the copper sheathings of
ships, giving the basic chloride $3Cu(OH)_2,CuCl_2,H_2O$, which is
found in nature as atakamite.

On account of its resistance to the action of acids, copper is

used for kettles, stills and evaporating pans, for covering roofs and ships' bottoms, and for coins. It furnishes also electrotype reproductions of medals, of engraved plates, of type, etc. (see p. 612). Great quantities of the metal are used for electrical wires and cables. Traces of other metals greatly reduce the conductivity. Thus arsenic amounting to 0.03 per cent lowers the conductivity about 14 per cent (see also p. 476).

The total world's production of copper in 1921 was 590,000 metric tons. This was considerably below the normal output, in consequence of over-production during the Great War. The banner year was 1917, when 1,425,000 metric tons were produced.

Alloys. — The qualities of copper are modified for special purposes by alloying it with other metals. **Brass** contains 18–40 per cent of zinc, and melts at a lower temperature (p. 155) than does copper. A variety with little zinc is beaten into thin sheets, giving Dutch metal ("gold leaf"). **Bronze** contains 3–8 per cent of tin, 11 or more per cent of zinc, and some lead. It was used for making weapons and tools before means of hardening iron were known, and later, on account of its fusibility, continued to be employed for castings until displaced largely by cast iron. **Gun metal** contains 10 per cent, and **bell metal** 20–24 per cent of tin. **German silver** contains 19–44 per cent of zinc and 6–22 per cent of nickel, and shows none of the color of copper.

Cupric Chloride $CuCl_2$. — This compound is made by union of copper and chlorine, or by treating the hydrate or carbonate with hydrochloric acid. The blue crystals of a **hydrate,** $CuCl_2$, $2H_2O$, are deposited by the solution. The **anhydrous salt** is yellow. Dilute solutions are blue, the color of cupric-ion, but concentrated solutions are green on account of the presence of the yellow molecules (p. 253). The aqueous solution is acid in reaction (p. 469). When excess of ammonium hydroxide is added to the solution, the basic chloride (see p. 603), which is at first precipitated, redissolves, and a deep-blue solution is obtained (see p. 607). This on evaporation yields deep-blue crystals of hydrated **ammonio-cupric chloride** $Cu(NH_3)_4.Cl_2,H_2O$. The deep-blue color of the solution, which is given by all cupric salts, is

that of ammonio-cupric-ion $Cu(NH_3)_4^{++}$. The dry salt also, absorbs ammonia, giving $CuCl_2,6NH_3$. Such compounds of ammonia with salts are extremely common, and are exactly analogous to hydrates. On reducing the partial pressure of ammonia above the salt, the compound is dissociated (compare p. 85).

Cuprous Chloride CuCl. — This salt may be made by boiling cupric chloride solution with hydrochloric acid and copper turnings:

$$CuCl_2 + Cu \rightarrow 2CuCl, \text{ or } Cu^{++} + Cu \rightarrow 2Cu^+.$$
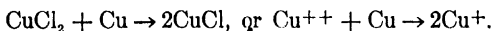
The solution contains compounds of cuprous chloride with hydrogen chloride, which are decomposed when the acid solution is diluted with water. Cuprous chloride itself is insoluble in water, and forms a white crystalline precipitate.

Cuprous chloride is hydrolyzed quickly by *hot* water, giving, finally, red, hydrated cuprous oxide, Cu_2O. It is dissolved by hydrochloric acid (see below). The solution is oxidized by the air, turning first brown and then green, and finally depositing the cupric oxychloride. It also has the power of absorbing carbon monoxide, to form a compound said to be $Cu(CO)Cl,H_2O$, and this property is used to separate this gas in analyzing, mixtures of gases. Cuprous chloride also dissolves (see p. 606) in ammonium hydroxide, giving **ammonio-cuprous chloride** $Cu(NH_3)_2.Cl$, the ion $Cu(NH_3)_2^+$ being colorless. The solution is quickly oxidized by the air, turns deep-blue, and then contains $Cu(NH_3)_4^{++}$.

The Bromides and Iodides of Copper. — By treatment of copper with bromine-water, and slow evaporation of the solution, jet-black crystals of anhydrous **cupric bromide** $CuBr_2$ are obtained (see p. 251). When dry cupric bromide is heated, bromine is given off, and **cuprous bromide** CuBr remains.

Cupric iodide CuI_2 appears to be unstable at ordinary temperatures. When a soluble iodide is added to a cupric salt, a white precipitate of **cuprous iodide** CuI and free iodine are obtained:

$$2Cu^{++} + 4I^- \rightleftharpoons 2CuI\downarrow + I_2.$$
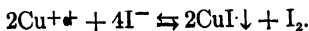
The Solution of Insoluble Salts when Complex Ions are Formed. — The solution of an insoluble salt liké cuprous chloride by hydrochloric acid or ammonium hydroxide is typical of a great variety of actions in whicʰ compound or complex ions are concerned. The explanation involves only principles already used in the previous discussion of ionic equilibria (pp. 569-578), and the student may find it advisable at this point to refresh his memory regarding these principles by re-reading the above pages very carefully.

The dissolving of cuprous chloride in ammonium hydroxide to form soluble ammonio-cuprous chloride $Cu(NH_3)_2.Cl$ will be considered in some detail as a typical case.

The **solubility product** of cuprous chloride in water is small; in other words, we cannot have a high concentration of Cu^+ ions and a high concentration of Cl^- ions simultaneously in the solution:

$$CuCl \text{ (solid)} \rightleftarrows CuCl \text{ (dissolved)} \rightleftarrows Cu^+_, + Cl^-. \qquad (1)$$
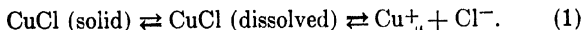
But when we add ammonium hydroxide (which is largely free ammonia NH_3, see p. 386) to a solution containing the very low amount of Cu^+ and Cl^- requisite to be in equilibrium with solid CuCl, the ammonia combines with the Cu^+ to form **complex ions** of the type $|Cu(NH_3)_2]^+$. The dissociation of these ions into Cu^+ and $2NH_3$ in the solution is exceedingly slight:

$$Cu^+ + 2NH_3 \rightleftarrows [Cu(NH_3)_2]^+. \qquad (2)$$

Hence the addition of ammonium hydroxide annihilates practically all of the Cu^+ ions in the solution. This disturbs the equilibrium represented in equation (1) above. To replace Cu^+, more CuCl must go into solution, and the process will continue, if enough ammonia is added, until all CuCl present has been dissolved.

The same exact laws of equilibrium used in discussing the dissolving of salts by acids (pp. 573-576) may be applied to the whole procedure. The principles involved are, as we shall find,

very extensively used in analysis (p. 714) and in industrial pro-
cesses (see p. 627).

The dissolving of cuprous chloride by hydrochloric acid is
explained in the same way. The only difference is that here the
copper is in complex *negative* ions such as $CuCl_2^-$. The dissocia-
tion of these ions into Cu^+ and $2Cl^-$ is also extremely slight:

$$CuCl_2^- \rightleftharpoons Cu^+ + 2Cl^-.$$
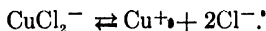
Consequently a solution in contact with solid CuCl, to which
hydrochloric acid is added, loses almost all of its Cu^+ ions,
and the salt necessarily dissolves in spite of its small solubility
product.

It must be noted very attentively that the dissolving of an
insoluble salt by the formation of a complex ion depends upon
two factors: (1) **the degree of insolubility of the salt,** and (2)
the stability of the complex ion. The more insoluble the salt
under consideration is, the more complete must be the removal
of one of the simple ions of this salt, by formation of a com-
plex ion, for solution to occur. For as soon as the degree of
dissociation of the complex ion is sufficient to give a concentra-
tion of the simple ion high enough to enable the solubility
product of the salt to be reached, it is impossible for more of
the salt to pass into solution.

The dissolving of insoluble cupric salts by ammonium hy-
droxide, already referred to on p. 604, is a good illustration of
this point. The deep-blue ion $[Cu(NH_3)_4]^{++}$ is very little dis-
sociated in solution:

$$[Cu(NH_3)_4]^{++} \rightleftharpoons Cu^{++} + 4NH_3.$$
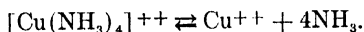
Addition of ammonium hydroxide to precipitates of cupric salts
results therefore in their complete solution, save only in the case
of *cupric sulphide.* This is, as we have already had occasion to
mention (p. 329), an *exceptionally insoluble salt.* Even the ex-
tremely small concentration of Cu^{++} in the solution which results
from the slight instability of the complex ammonio-cupric ion
suffices, therefore, *after the merest trace of CuS has been dis-
solved,* to bring the product of the concentrations of Cu^{++} and

Cupric Oxide CuO. — When the liquid containing the blue precipitate of cupric hydroxide is boiled, the blue color changes to *black,* and cupric oxide is thrown down:

$$Cu(OH)_2 \rightarrow CuO + H_2O.$$
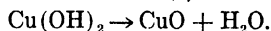
This oxide is used in the laboratory to ascertain the compositions (and formulæ) of organic compounds **(determination of carbon and hydrogen).** A weighed amount of the organic compound is placed in a horizontal tube, between heated masses of the oxide. A stream of oxygen or air carries the vapor of the organic compound over the cupric oxide, which oxidizes it to water and carbon dioxide. The first is absorbed in a weighed **U**-tube filled with calcium chloride, and the second is caught in a weighed vessel containing potassium hydroxide. From the increase in weight in each case, the corresponding weights of hydrogen and carbon (derived from the weighed portion of the organic compound) are calculated.

Cupric Nitrate $Cu(NO_3)_2,6H_2O$. — The nitrate is made by treating cupric oxide or copper with nitric acid (p. 397), and is obtained from the solution as a deliquescent, crystalline **hexahydrate.** When dehydrated at 65° the salt is partly hydrolyzed, and a basic nitrate $Cu_4(OH)_6(NO_3)_2$ remains.

Carbonate of Copper. — No normal carbonate ($CuCO_3$) can be obtained. A **basic carbonate** (malachite) is found in nature and is precipitated by adding soluble carbonates to cupric salts:

$$2CuSO_4 + 2Na_2CO_3 + H_2O \rightarrow Cu_2(OH)_2CO_3 + 2Na_2SO_4 + CO_2.$$
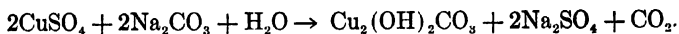
The carbonate, if formed, would be hydrolyzed by water **(p. 470).**

Cyanides of Copper. — With potassium cyanide and a solution of a cupric salt, **cupric cyanide** $Cu(NC)_2$ is precipitated. This is not stable, however, and gives off cyanogen, leaving **cuprous cyanide** CuNC:

$$2Cu(NC)_2 \rightarrow 2CuNC + C_2N_2.$$
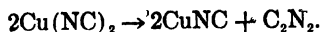
Cuprous cyanide is insoluble in water, but interacts with an ex-‍cess of potassium cyanide solution, producing a colorless liquid, from which $K.Cu(CN)_2$, **potassium cuprocyanide**, may be obtained in colorless crystals. The complex anion $Cu(CN)_2^-$ is so little ionized to Cu^+ and $2CN^-$ that all insoluble copper compounds, *including cupric sulphide*, are dissolved by potassium cyanide; and none of them can be precipitated from the solution. Zinc is actually unable to displace copper from such a solution (see pp. 655, 659).

Cupric Acetate. — By the oxidation of plates of copper, separated by cloths saturated with acetic acid (vinegar), a basic acetate of copper (**verdigris**) is obtained:

$$6Cu + 8HC_2H_3O_2 + 3O_2 \rightarrow 2Cu_3(OH)_2(C_2H_3O_2)_4 + 2H_2O.$$
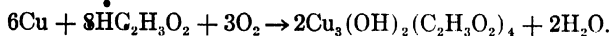
It is used in manufacturing green paint, is insoluble in water, and is unaffected by light. It dissolves in acetic acid, and green crystals of the **normal acetate** $Cu(C_2H_3O_2)_2.H_2O$ are obtained from the solution. The basic acetate is used in preparing **Paris green**, employed in the extermination of potato-beetles and other insects and for the destruction of parasitic fungi.

Analytical Reactions of Compounds of Copper. — The ion of ordinary cupric salts, cupric-ion Cu^{++}, is blue, and that of cuprous salts, cuprous-ion Cu^+, is colorless. Cuprous solutions, however, are easily oxidized by the air and become blue. In solutions containing cupric-ion, hydrogen sulphide precipitates cupric sulphide, even in presence of acids (p. 578). Bases throw down the blue hydroxide, and carbonates precipitate a green basic salt (p. 247). Potassium ferrocyanide gives the brown, gelatinous **cupric ferrocyanide**:

$$2Cu.SO_4 + K_4.Fe(CN)_6 \rightleftarrows Cu_2.Fe(CN)_6 \downarrow + 2K_2SO_4.$$
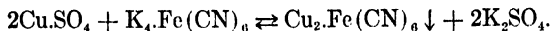
A characteristic test is the formation of the deep-blue $Cu(NH_3)_4^{++}$ ion with excess of ammonium hydroxide. This solution itself responds to certain precipitants only (*e.g.*, H_2S). Solutions of complex cuprous cyanides such as $K.Cu(CN)_2$ are

'colorless, and do not respond to any of the above tests. With microcosmic salt or borax (pp. 413, 456), copper compounds form a bead which is blue in the oxidizing part of the flame and becomes red and opaque (liberation of copper) in the reducing flame.

More active metals, such as zinc or iron, displace copper from solutions of its salts, so that a blade of a knife, for example, receives instantly a red coating of copper when immersed in such a solution:

$$Fe + Cu^{++} \rightarrow Fe^{++} + Cu \downarrow .$$
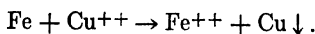
Copper Plating. — When platinum or carbon plates, connected with a battery, are immersed in a solution of cupric sulphate, copper is deposited on the negative plate (cathode). The $SO_4^=$ migrates towards the positive plate (anode) and there produces oxygen and sulphuric acid:

$$2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + O_2 \uparrow .$$
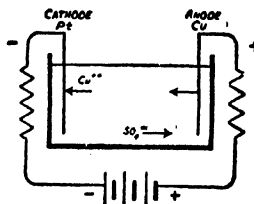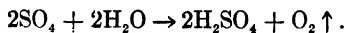
If the anode is made of copper itself, however, the $SO_4^=$ migrates, but is not discharged. Instead, copper goes into solution (Fig. 128) as Cu^{++}, in amount equal to that deposited on the other plate. Thus the quantity of cupric sulphate in solution remains

Fig. 128.

unchanged, and the effect is, virtually, to transfer copper from the copper anode to the cathode.

Electrotypes. — A copper electrotype of an object like a medal is made by first preparing a cast of the medal in plaster of Paris or wax. The surface of this is rubbed with graphite, to render it a conductor, and the cast is used as the cathode in a cell like that just described. The deposit of copper, when stripped off, is found to show an exact reproduction of the engraving, etc., on the object.

Book plates are made by taking a cast of each page of type, preparing the copper electrotype, and then strengthening and

thickening it by filling the back with melted lead. The printing
is then done from the electrotype. For newspapers this process
is too slow, and the plate is made from the cast by means of
melted stereotype-metal (lead, antimony, tin; 82 : 15 : 3).

Copper Refining. — The copper, as obtained from the ores by
the treatment already described (p. 602), contains a certain
amount of silver, gold, and baser metals. The former pay for
the cost of refining, and the simultaneous
removal of the latter gives pure copper
suitable for electrical purposes.

The principle is the same as that used
in electroplating. The heavy plates of
poled copper (p. 603) are hung at inter-
vals in large, lead-lined vats of copper
sulphate solution and form the anodes
(Fig. 129, diagrammatic, view from
above). The metal is deposited on thin
sheets of copper, which are coated with
graphite to permit the deposit to be easily
stripped off. These sheets hang in the
vat between the anodes, and are connected
with the negative wire. The copper, along with such traces of
more active metals, like zinc, as are present, is ionized and goes
into solution, until the anode is reduced to a skeleton and is
exchanged for a fresh one. The less active metals, such as silver
and gold, as well as traces of sulphides, are not ionized. They
fall to the bottom of the vat, as a sort of heavy mud. At the
cathode copper ions alone are discharged and deposited, because
copper is the least active of the metals present in ionic form.
In this way copper, 99.8 per cent pure, can be obtained, and gold
and silver are recovered from the mud.
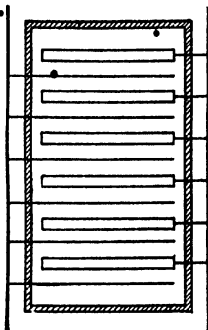
FIG. 129.

MERCURY Hg

Chemical Relations of the Element. — Like copper, **mercury**
(Hg, at. wt. 200.6) enters into **two series** of compounds, namely
the **mercurous Hg^I** and the **mercuric Hg^{II}**. The mercurous
halides, like the cuprous halides, are insoluble in water and are

decomposed by light. Both of the oxides, Hg_2O and HgO, are basic exclusively, but in a feeble degree. The hydroxides, like silver hydroxide (p. 623), are not stable, and lose water, giving the oxides. The salts of both sets are markedly hydrolyzed by water, and basic salts are therefore common. Mercury enters into the anions of a number of complex salts, such as $HgCl_4^=$, $HgI_4^=$, $Hg(CN)_4^=$, etc. It forms a class of ammono-basic mercury compounds, like $_2Hg^{II}NH_2Cl$, all of which are insoluble.

The mercury salts of volatile acids, like the corresponding salts of ammonium (p. 386), can all be volatilized completely. Mercury vapor and all mercury compounds are **poisonous**, the soluble ones more markedly so than the insoluble ones.

Occurrence and Isolation of the Metal. — Mercury occurs native and to a larger extent as red, crystalline cinnabar, mercuric sulphide HgS. The chief mines are in Spain, Italy, and California.

The liberation of the metal is easy, because, when roasted, the sulphide is decomposed, and the sulphur forms sulphur dioxide. The mercury does not unite with the oxygen, for the oxide decomposes (p. 19) when heated:

$$HgS + O_2 \rightarrow Hg + SO_2.$$
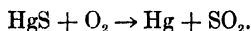
In some places the ore is spread on perforated brick shelves in a vertical furnace, and the gases pass through tortuous flues in which the vapor of the metal condenses.

The metal is sold in iron flasks, containing 75 pounds. The world's production averages 100,000 flasks a year.

Physical Properties. — Mercury is a silver-white liquid at ordinary temperatures, hence its name, quicksilver (*i.e.*, live silver). At $-38.7°$ it freezes, and at $357°$ it boils. The vapor density shows the molecules to be monatomic.

On account of its high specific gravity (13.6, at $0°$) and low vapor tension, the metal is employed for filling barometers. Its uniform expansion favors its use in thermometers. It forms amalgams with all the familiar metals, with the exception of iron and platinum.

Chemical Properties. — When kept at a temperature near to its boiling-point, mercury combines slowly with oxygen. Mercury does not displace hydrogen from dilute acids (p. 240), but with oxidizing acids like nitric acid and hot concentrated sulphuric acid, the nitrates and sulphate (mercuric) are formed. With excess of mercury, mercurous nitrate, and with excess of the hot acid, mercuric nitrate, are produced. When mercury is divided into minute droplets, with relatively large surface, it is used in medicine ("blue pills"), and shows an activity which is entirely wanting in larger masses.

The Halides of Mercury. — **Mercurous chloride** HgCl (calomel) is obtained as a white powder by precipitation. It is made by subliming mercuric chloride with mercury:

$$HgCl_2 + Hg \rightleftarrows 2HgCl,$$

or more usually by subliming a mixture of mercuric sulphate, made as described above, with mercury and common salt. It is deposited on the cool part of the vessel as a fibrous crystalline mass. Its vapor is dissociated entirely into mercury and mercuric chloride. The substance is used in medicine on account of its tendency to stimulate all organs producing secretions.

By direct union with chlorine, **mercuric chloride** $HgCl_2$ (**corrosive sublimate**) is formed. It is usually manufactured by subliming mercuric sulphate with common salt, and crystallizes in white, rhombic prisms. It melts at 265° and boils at 307°. The solubility at 20° is 7.4 parts in 100 of water. The aqueous solution is slightly acid in reaction. The salt is easily reduced to mercurous chloride. When excess of stannous chloride is added to the solution, the white precipitate of calomel, first formed, passes into a heavy gray precipitate of finely divided mercury:

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2HgCl,$$
$$2HgCl + SnCl_2 \rightarrow SnCl_4 + 2Hg.$$
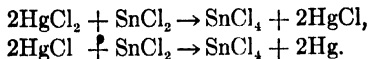
Corrosive sublimate, when taken internally, is extremely poisonous. A very dilute solution (1 : 1000) is used in surgery to destroy lower organisms and thus prevent infection of wounds.

Mercuric chloride acts also as a preservative of zoölogical materials, forming insoluble compounds with proteins, and preventing decay. For the same reason, albumen (white of an egg) is given as an antidote in cases of sublimate poisoning.

The Oxides. — When bases (excepting ammonium hydroxide, see p. 617) are added to solutions of mercurous salts, the greenish-black mercurous oxide Hg_2O is thrown down. Under the influence of light or gentle heat (100°), this oxide resolves itself into mercuric oxide and mercury.

Mercuric oxide HgO is formed as a red, crystalline powder, when mercury is heated in air near to 357°, but is usually made by decomposing the nitrate. It is formed also as a yellow powder by adding bases (excepting ammonium hydroxide, see p. 617) to solutions of mercuric salts.

Other Salts of Mercury. — **Mercurous nitrate** $HgNO_3,H_2O$ is formed by the action of cold, diluted nitric acid upon *excess* of mercury. It is hydrolyzed, slowly by cold, and rapidly by warm water, giving an insoluble basic nitrate:

$$2HgNO_3 + H_2O \rightleftharpoons HNO_3 + Hg_2(OH)NO_3 \downarrow .$$

On this account a clear solution can be made only when some nitric acid is added. Free mercury is also kept in the solution to reduce mercuric nitrate, which is formed by atmospheric oxidation:

$$Hg(NO_3)_2 + Hg \rightarrow 2HgNO_3, \quad \text{or} \quad Hg^{++} + Hg \rightarrow 2Hg^{+}.$$

Mercuric nitrate $Hg(NO_3)_2,8H_2O$ is produced by using excess of warm, concentrated nitric acid with mercury. The aqueous solution is strongly acid, and deposits a yellowish, crystalline, basic nitrate $Hg_3(OH)_2O(NO_3)_2$. The hydrolysis is reversed by adding nitric acid.

Mercurous sulphide Hg_2S is formed by precipitation from mercurous salts, but decomposes into mercury and mercuric sulphide.

Crystallized **mercuric sulphide** HgS occurs as cinnabar, and is red. When formed by precipitation with hydrogen sulphide, or by rubbing together mercury and sulphur, it is black and amor-

phous. By sublimation, in the course of which it dissociates and recombines, the black form gives the red, crystalline one.

The black and the red varieties do not interact with concentrated acids, or even with boiling nitric acid, which oxidizes most sulphides readily. They are, therefore, still less soluble than is cupric sulphide (pp. 578, 607). They are attacked, however, by *aqua regia*, because of the formation of the negative ion (compare gold, p. 628) of a complex acid $H_2.HgCl_4$. The red form of the sulphide is used in making paint (**vermilion**).

• **Mercuric fulminate** $Hg(ONC)_2$ is obtained as a white precipitate when mercury is treated with nitric acid and alcohol is added to the solution. It decomposes suddenly when struck, and is used in making percussion caps and detonators.

Ammono-Compounds of Mercury. — When ammonium hydroxide is added to a solution of a mercuric salt, a white substance, of a type which we have not previously encountered, is thrown down. • Mercuric chloride gives $Hg(NH_2)Cl$, commonly called "infusible white precipitate," or •**ammono-basic mercuric chloride.** •

$$HgCl_2 + H.NH_2 + NH_3 \rightarrow Hg(NH_2)Cl + NH_4Cl.$$
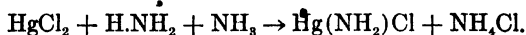
The action is similar to an hydrolysis which gives a basic salt: $HgCl_2 + H.OH \rightarrow Hg(OH)Cl + HCl$, excepting that ammonia, $H.NH_2$ plays the part of the water. Water gives aquo-basic salts. When liquid ammonia is the solvent, ammono-basic salts are produced. In a few cases, as here, an ammono-basic salt is obtained even when water is present. The study of reactions in liquid ammonia solutions by E. C. Franklin has led to the discovery of a large number of new and most interesting substances.

When calomel is treated with ammonium hydroxide, it turns into a black, insoluble body. This is a mixture of free mercury, to which it owes its dark color, and "infusible white precipitate," $Hg + Hg(NH_2)Cl$. To this reaction calomel owes its name (Greek, καλομέλας, beautiful black).

Analytical Reactions of Mercury Compounds. — The two ionic forms of the element, mercurous-ion $Hg+$ and •mercuric-ion

Hg^{++}, are both colorless. Their chemical behavior is entirely different. Both give the black sulphide HgS, which is insoluble in acids and other solvents of mercury salts. Mercurous-ion gives an insoluble, white chloride, a black oxide, and a black mixture with ammonium hydroxide. Mercuric-ion gives a soluble chloride, a yellow, insoluble oxide, and a white precipitate with ammonium hydroxide. The behavior with stannous chloride (p. 615) is characteristic.

More active metals displace mercury from all compounds. Copper is used as the displacing metal, in testing for Hg^+ or Hg^{++}, because the silvery mercury is easily seen on its surface.

Salts of mercury are volatile. When heated in a tube with sodium carbonate, they give a sublimate of metallic mercury.

Exercises. — 1. Make an equation: (a) for the oxidation of ethyl alcohol by heated cupric oxide; (b) for the precipitation of cupric sulphide from cupric sulphate solution.

2. When we electrolyzed sodium chloride solution (p. 169), hydrogen was liberated at the cathode. What principle, used in the electrolytic refining of copper, does this phenomenon illustrate?

3. How could you recognize cupric sulphate solution by showing that it contained, (a) cupric-ion, (b) sulphate-ion (p. 346)?

4. Formulate the action of potassium cyanide in dissolving cupric hydroxide and cuprous sulphide, assuming that potassium cuprocyanide is formed.

5. How should you set about making cupric orthophosphate, ammonium cuprocyanide, and lead cuprocyanide?

6. Write the formulæ of some double salts analogous to potassium-cupric sulphate (p. 609).

7. What chemical reagents are present in a Bunsen flame? If borax beads were made in the oxidizing flame with cupric chloride, cuprous bromide, and cupric sulphate, severally, what actions would take place?

8. Which is the more stable complex ion, $[Cu(CN)_2]^-$ or $[Cu(NH_3)_4]^{++}$? Justify your answer in detail.

9. Formulate, by each of the two methods discussed on pp.

301-305, complete equations for the various oxidation and re-
duction reactions mentioned in this chapter.

10. Formulate ionic equations to explain, (a) why a red pre-
cipitate is obtained when an equivalent quantity of potassium
iodide solution is added to a soluble mercuric salt, and (b) why
this precipitate redissolves when an excess of potassium iodide
is added (p. 614).

CHAPTER XLIV

ALTHOUGH the metals considered in this chapter are located in widely separated groups of the periodic system, they form a natural family of "noble metals."

SILVER Ag

Chemical Relations of the Element. — Silver (Ag, at. wt. 107.88) presents a curious assortment of chemical properties. It ·differs from copper in having a strongly basic oxide, and in giving salts with active acids which are not hydrolyzed by water. In these respects it approaches the metals of the alkalies and alkaline earths. It resembles copper in entering into complex compounds, and in giving insoluble halides. It resembles gold and platinum, in that its oxide is easily decomposed by heat, and in the low position it occupies in the electromotive series and the consequent slight chemical activity of the free metal.

Occurrence. — Native silver, usually scattered through a rocky matrix, contains varying amounts of gold and copper. Native copper always contains dissolved silver. Sulphide of silver (Ag_2S) occurs alone and dissolved in galenite (PbS). The chief supplies come from the Rocky Mountains, Ontario, and Mexico.

Metallurgy. — The silver contained free, or as sulphide, in ores of copper and lead, is found in the free state dissolved in the metals extracted from these ores, and is secured by refining them. In the electrolytic refining of copper, silver is obtained from the mud deposited in the baths (p. 613). The proportion present in lead is usually small. **Parke's process,** by which the silver is separated from the lead, takes advantage of the fact that molten zinc and lead are practically insoluble in one an-

620

other, while silver is much more soluble in zinc than in lead. The principle is the same as in the removal of iodine from water by ether (p. 158). The lead is melted and thoroughly mixed by machinery with a small proportion of zinc. After a short time the zinc floats to the top, carrying with it almost all of the silver, and solidifies at a temperature at which the lead is still molten. The zinc-silver alloy, largely a compound Ag_2Zn_5, is skimmed off, and heated moderately in a furnace to permit the adhering lead to drain away. The zinc is finally distilled off in clay retorts, and any lead remaining with the silver is removed by **cupellation**. This operation consists in heating the molten metal strongly in a blast of air. The lead is converted into litharge (PbO), which flows in molten condition over the edge of the cupel, and the silver is then cast.

Ores of silver which do not contain much or any lead are often smelted with lead ores, and the product is treated as de-. scribed above, but many other processes are in use. The gold, which goes with the silver in Parke's process, is separated electrolytically (p. 613). Plates of the silver-gold alloy form the anode, and silver nitrate solution the vat-liquid. The silver, being the more active metal, is ionized and deposited on the cathode, while the gold collects as a powder in a bag surrounding the anode.

The world's total output of silver in 1921 was 168,000,000 ounces (troy). The mines of the United States produced 63,-000,000 ounces, and those of Mexico 50,000,000.

Physical Properties. — Pure silver is almost perfectly white. It melts at 960°. Its sp. gr. is 10.5. Its ductility is such that wires can be drawn so fine that 2 kilometers weigh only about 1 g. In the molten condition it dissolves about twenty-two times its own volume of oxygen, but gives up almost all of this as it solidifies. Fantastically irregular masses result from the "sprouting" or "spitting" which accompanies the escape of the gas.

When an electric discharge passes between the ends of two silver wires, held under water, silver is dispersed at the points and forms a *colloidal suspension*. The color of the solution varies from brownish to pink, according to the conditions. Col-

loidal suspensions of gold and of platinum can be made in the same way.

For use in silver ware and coins the metal is alloyed with copper to make it harder. American coins contain 90 per cent of silver ("900 fine"). British coins formerly contained 92.5 per cent, which is the proportion in sterling silver, but the rise in price of the metal has recently necessitated a reduction to 50 per cent.

Chemical Properties. — Silver, when cold, is oxidized by ozone, but not by oxygen (see silver oxide). It does not displace hydrogen from aqueous solutions of acids. Sulphur compounds in the air tarnish the surface, producing Ag_2S, as do also eggs, secretions from the skin (proteins, p. 511), and vulcanized rubber. Silver interacts with cold nitric acid and with hot, concentrated sulphuric acid, giving the nitrate or sulphate of silver and oxides of nitrogen or of sulphur (pp. 397, 346).

The Halides of Silver. — The chloride AgCl, bromide AgBr, and iodide AgI are formed as curdy precipitates when a salt of silver is added to a solution containing the appropriate halide ion. The first is white, and melts at about 457°. The second and third are very pale-yellow and yellow respectively. The insolubility in water increases in the above order.

When exposed to light, the chloride becomes first violet (colloidal silver, dispersed in the AgCl) and finally brown, chlorine being liberated. The bromide and iodide behave similarly. Solid silver chloride absorbs ammonia, forming at low pressures $2AgCl,-3NH_3$, and with higher pressures of ammonia $AgCl,3NH_3$ (compare p. 605).

Complex Compounds of Silver. — Silver chloride dissolves easily in excess of ammonium hydroxide, giving the complex cation $Ag(NH_3)_2{}^+$. The bromide, which is less readily soluble, gives the same complex-ion. The iodide is hardly soluble at all in ammonium hydroxide, and can be precipitated in ammoniacal solution. All three of the insoluble halides interact with solutions of potassium cyanide and of sodium thiosulphate, and go into solution, as do also all the other insoluble silver salts. With

the cyanide, double decomposition gives first the insoluble silver cyanide AgCN, which then dissolves, forming the soluble **potassium argenticyanide** K.Ag(CN)$_2$. The thiosulphate gives a solution containing the complex salt Na$_3$.Ag(S$_2$O$_3$)$_2$.

The more active metals, like zinc and copper, displace silver from all solutions, whether the solutions contain simple or complex salts.

Oxides of Silver. — When sodium hydroxide is added to a solution of a salt of silver, a pale-brown precipitate is obtained, which, after being freed from water, is found to be **argentic oxide** Ag$_2$O, and not AgOH. The aqueous solution of argentic oxide, however, is distinctly alkaline, and presumably therefore does contain the hydroxide: 2AgOH $\rightleftarrows$ Ag$_2$O + H$_2$O. It is an active basic oxide. When moist, it absorbs carbon dioxide from the air. With ammonium hydroxide it forms the soluble Ag(NH$_3$)$_2$.OH. When the oxide is heated, it gives off oxygen, leaving metallic silver.

Silver **peroxide** Ag$_2$O$_2$ is formed by the action of ozone on silver. In the electrolysis of silver nitrate a deposit of shining black crystals which contain some silver peroxide is formed on the anode.

Salts of Silver. — Silver nitrate AgNO$_3$ is obtained by treating silver with aqueous nitric acid:

$$3Ag + 4HNO_3 \rightarrow 3AgNO_3 + NO + 2H_2O.$$

From the solution, colorless rhombic crystals are deposited. These melt at 208.6°. Thin sticks made by casting (lunar caustic) are used to cauterize sores, because the substance combines with proteins to form insoluble compounds. The aqueous solution is *neutral*. The pure salt is not affected by light, but when deposited on cloth, on the skin of the fingers, or on the mouth of the reagent bottle, it is reduced by organic matter, and silver is liberated. For this reason it is an ingredient in some marking-inks.

Silver carbonate, the neutral salt Ag$_2$CO$_3$, and not a basic carbonate, is precipitated from solutions of salts of silver by

soluble carbonates. It is slightly yellow in color. With water it gives a faint alkaline reaction and, like calcium carbonate, is soluble in excess of carbonic acid (p. 501). When heated, the carbonate decomposes, leaving metallic silver. The **sulphate** Ag_2SO_4 is made by the action of concentrated sulphuric acid on the metal. When it is mixed with a solution of aluminium sulphate (see p. 585) octahedral crystals of **silver-alum** Ag_2SO_4,-$Al_2(SO_4)_3,24H_2O$ are obtained. **Silver sulphide** Ag_2S is precipitated by hydrogen sulphide from solutions of all silver compounds, whether free acids are present or not, and irrespective of the form in which the silver is combined. *Excess* of potassium cyanide, however, prevents its precipitation from the argenticyanide. The sulphide is formed by the action of metallic silver on alkaline hydrosulphides, and this interaction forms the basis of the "hepar" test for sulphur. Silver **orthophosphate** Ag_3PO_4 (yellow), **arsenate** Ag_3AsO_4 (brown), and **chromate** Ag_2CrO_4 (crimson) are produced by precipitation, and their distinctive colors enable us to use silver nitrate in analysis as a reagent for identifying the acid radicals.

Electroplating. — The process is similar to the electro-deposition of copper (p. 612). The article to be plated is cleaned with extreme care and attached to the negative wire. A plate of silver forms the positive electrode and, since simple salts of silver do not give coherent deposits, the bath is a solution of potassium argenticyanide. The potassium-ion K^+ migrates to the negative wire and, since potassium requires a much greater electromotive force for its liberation than does silver, silver is there deposited from the trace of argentic-ion given by the complex silver ions in the neighborhood:

$$Ag(CN)_2^- \leftrightarrows Ag^+ + 2CN^-, \quad Ag^+ + \ominus \rightarrow Ag^0.$$

At the positive electrode silver goes into solution in equivalent amount, giving argentic-ion, and the above equations are reversed.

Mirrors are silvered through the reduction of ammonio-silver nitrate by organic compounds such as formaldehyde CH_2O (formalin), or grape sugar:

$$4AgOH + CH_2O \rightarrow 3H_2O + 4Ag\downarrow + CO_2.$$
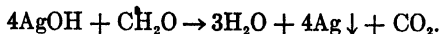
The film of silver is washed, dried, and varnished.

Photography. — The taking of a photograph involves four processes — preparation of the plate, exposure, development, and fixing.

In preparing the plate, silver bromide is first precipitated in water containing gelatine. The mixture is kept warm, to permit the precipitate to become more sensitive to light by acquiring a coarser grain ("ripening"). The "emulsion" is applied to plates of glass or strips of transparent celluloid (films).

The brief **exposure** of the plate to the image of the object, well-focussed in the camera, produces no visible effect. But the bromide is thereafter more easily reduced to metallic silver, in proportion to the intensity of the light that fell upon each part.

Development consists in applying a reducing agent, of such slight activity that its effect during the process on non-illuminated parts of the bromide is practically zero. Ferrous oxalate, or an alkaline solution of pyrogallol $C_6H_3(OH)_3$ or of quinol $C_6H_4(OH)_2$ (two substances belonging to the class of phenols, see p. 441), may be used. The reduction goes fastest and deposits most silver where the illumination was most intense: Thus, the plate becomes most opaque where the object was brightest, and *vice versa*. On account of this reversal, the plate is called a *negative*. With the potassium salt of quinol, quinone $C_6H_4O_2$ is formed:

$$2AgBr + C_6H_4(OK)_2 \rightarrow 2Ag + 2KBr + C_6H_4O_2.$$
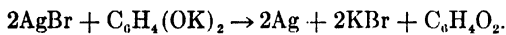
The foregoing processes are all carried out in a faint red light, which is almost without action on silver bromide. To prevent the gradual reduction of the remaining, unchanged bromide to silver by daylight, it is dissolved out by soaking the plate in sodium thiosulphate (**fixing**). The plate is now *clear* where no silver was deposited. The negative is finally washed thoroughly to remove all except the gelatine and the silver image, and is then dried.

. In **printing,** the prepared paper is illuminated *through* the negative, and light and dark are again reversed. The denser parts of the negative protect the paper below them, and leave these parts white. On *printing paper*, silver chloride suspended in egg albumen is the sensitive substance, and the silver is liberated in a reddish, colloidal condition. The color is improved by *toning* with a solution containing gold chloride, as part of the silver goes into solution and gold (purplish) is deposited in its place. The print is fixed with hypo, washed, and dried. *Papers* like velox (invented by Baekeland) are essentially like plates (silver bromide in gelatine), and are exposed, developed, and fixed in the same way.

Analytical Reactions of Silver Compounds. — Argentic-ion Ag^+ is colorless. Many of its compounds are insoluble, the precipitation of the chloride, which is insoluble in dilute acids, being used as a test. Mercurous chloride and lead chloride are also white and insoluble, but silver chloride dissolves in ammonium hydroxide, mercurous chloride turns black, and lead chloride is not altered in color (and is also soluble in hot water). With excess of ammonium hydroxide, silver salts give the complex cation $Ag(NH_3)_2^+$ and, from solutions containing silver in this form, only the iodide and sulphide can be precipitated. Sodium thiosulphate and potassium cyanide dissolve all silver salts, giving salts of complex acids with silver in the anion (p. 623).

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GOLD Au

Chemical Relations of the Element. — Gold (Au, at. wt. 197.2) forms two very incomplete series of compounds corresponding respectively to aurous and auric oxides, Au_2O and Au_2O_3. The former is a feebly basic oxide, the latter mainly acid-forming. No simple salts with oxygen acids are stable. All the compounds of gold are easily decomposed by heat with liberation of the metal. All other common metals displace gold from solutions of its compounds (p. 240). Mild reducing agents likewise liberate gold. The element enters into many complex anions.

Occurrence and Metallurgy. — Gold is found chiefly in the free condition, disseminated in veins of quartz, or mixed with alluvial sand. Small quantities are found also in sulphide ores of iron, lead, and copper. Telluride of gold (sylvanite), in which silver takes the place of a part of the gold $[Au,Ag]Te_2$, is found in Colorado.

In vein mining (*e.g.*, in the Transvaal) the rock is pulverized with iron stamps working in an iron trough. The powder is washed in the form of mud over plates of copper amalgamated with mercury, in which about 55 per cent of the gold dissolves. The amalgam is afterwards scraped off, the mercury removed by distillation, and the gold residue refined. The tailings still contain 45 per cent of the gold, adhering to the particles of rock. They are covered with sodium cyanide solution, and exposed to the air, until the gold has been dissolved as sodium aurocyanide $NaAu(CN)_2$. From this solution the gold is deposited by electrolysis, or displaced by zinc.

The alluvial deposits are washed, on a small scale, in "cradles" (shallow pans) and, on a large scale, by being carried by water down a long trough (**placer mining**). The gold, having a much higher specific gravity than the rock, sinks to the bottom, while the rock particles are carried away. In the trough the gold settles between cleets nailed across the bottom. In **hydraulic mining**, a modification of placer mining, very heavy streams of water are thrown against the deposit.

In 1920, the gold production of the world exceeded $330,-000,000 in value. $165,000,000 of this came from the Transvaal, and $50,000,000 from the United States. In 1912 the world yield was $475,000,000, but the increase in the cost of working has caused many mines to be shut down.

Properties. — Gold is yellow in *color*. It is the most *malleable* and *ductile* of metals. It *melts* at 1075°. To enable it to resist wear, it is alloyed with copper. Pure gold is "24 karat" fine. British gold coins are 22 karat, and American coins 21.6 karat (90 per cent gold).

Gold is not affected by free oxygen nor by hydrogen sulphide. It does not displace hydrogen from dilute acids, nor does it inter-

act with nitric or sulphuric acids or any oxygen acids except selenic acid. It combines, however, with free chlorine and bromine. It interacts with a mixture of nitric and hydrochloric acids (*aqua regia*), giving chloraurfic acid $H.AuCl_4$. This happens, not because *aqua regia* is more active than are any of the substances it contains, but because it furnishes both the chlorine and the chloride-ion Cl^- required to produce the exceedingly stable (little dissociated) anion $AuCl_4^-$. Chlorine-water dissolves it also, for the same reason (see p. 398). Gold is the least active of the familiar metals.

Compounds with the Halogens. — **Chlorauric acid,** formed as above, is deposited in yellow, deliquescent crystals of $H.AuCl_4,4H_2O$. The yellow sodium chloraurate $NaAuCl_4,2H_2O$ obtained by neutralization of the acid, is used in photography (p. 626). The acid gives up hydrogen chloride when heated very gently, leaving the red, crystalline **auric chloride** $AuCl_3$. When auric chloride is heated to 180°, **aurous chloride** $AuCl$ and chlorine are formed.

Other Compounds. — When caustic alkalies are added to chlorauric acid, or to sodium chloraurate, **auric hydroxide** $Au(OH)_3$ is precipitated. This substance is a weak acid, and interacts with excess of the base, forming **aurates. Auric oxide** Au_2O_3 is a brown, and **aurous oxide** Au_2O is a violet powder. On account of its reducing action, hydrogen sulphide precipitates from chlorauric acid a dark-brown mixture containing much **aurous sulphide** Au_2S and free sulphur, as well as some **auric sulphide** Au_2S_3.

The **aurocyanides** like $K.Au(CN)_2$, and the **auricyanides,** like $K.Au(CN)_4$, are formed by the action of potassium cyanide on aurous and auric compounds, respectively. They are colorless and soluble. Their solutions are used as baths, in conjunction with a gold anode, for electro-gilding.

It will be seen that gold, although physically a metal, is chemically on the whole a *non-metallic* element.

Assaying. — In assaying a sample to determine its gold content, the finely-crushed material is heated with borax and lead

in a small crucible (cupel) of bone ash. The lead and copper. are oxidized, and their oxides are absorbed by the cupel, leaving a drop of molten alloy of gold and silver. The cold button is flattened by hammering and rolling, and treated with nitric acid to remove the silver. The gold, which remains unattacked, is washed, fused again, and weighed. The acid will not interact with the silver, and remove it completely, if the quantity of gold exceeds 25 per cent. When the proportion of gold is greater than this, a suitable amount of pure silver is fused with the alloy ("quartation").

The principles behind quartation have recently been elucidated by Tammann, as the result of a study of the crystal structure of gold-silver alloys. Both of these metals exhibit a cubic-lattice arrangement of atoms (see p. 106) and form solid solutions with each other by orderly replacement of atoms in the unit cubes. Now if gold constitutes *more than one-quarter* of the atoms in such a cubic lattice, then, after the surface silver atoms have been removed by an acid, there will remain a "united front" of gold atoms, which prohibits further corrosion. But if *less than one-quarter* of the atoms are gold, the formation of a coherent barrier is impossible, and the alloy will be completely disintegrated by the acid.

The Platinum Metals

The rarer elements of Mendelejeff's eighth group divide themselves into sets of three each. **Ruthenium** (Ru, at. wt. 101.7), **rhodium** (Rh, at. wt. 102.9), and **palladium** (Pd, at. wt. 106.7) have specific gravities from 12.26 to 11.5. Similarly **osmium** (Os, at. wt. 190.9), **iridium** (Ir, at. wt. 193.1), and **platinum** (Pt, at. wt. 195.2) form a triad with specific gravities from 22.5 to 21.5. Chemically, ruthenium shows the closest resemblance to osmium, and both are allied to iron. Similarly, rhodium and iridium, and palladium and platinum are natural pairs.

The six elements are found alloyed in nuggets and particles which are separated from alluvial sand by washing. Platinum forms 60–84 per cent of the whole. The chief deposits are in the Ural Mountains, smaller amounts being found in Colombia, Cali-

fornia, Australia, Borneo, and elsewhere. The components are separated by a complex series of chemical operations.

Ruthénium and Osmium. — These metals are gray like iron, while the other four are whiter and more like cobalt and nickel. They also resemble iron in being the most infusible members of their respective sets. Both melt considerably above 2000°. They likewise resemble iron in uniting easily with free oxygen, while the other four elements do not. Ruthenium gives RuO_2 and even RuO_4, although the latter oxide is more easily obtained indirectly. Osmium gives OsO_4, "osmic acid," a white crystalline body melting at 40° and boiling at about 100°. The odor and irritating effects of the vapor recall chlorine (Greek, ὀσμή, odor). The substance is not really an acid, nor even an acid anhydride. The aqueous solution is used in histology, and stains tissues in consequence of its reduction by organic bodies to metallic osmium. Osmium forms also a yellow, crystalline **fluoride**, OsF_8 (m.-p. 34.5°). It will be observed that ruthenium and osmium have a maximum valence of eight.

Rhodium and Iridium. — These metals are not attacked by *aqua regia,* while the other four are dissolved, more or less slowly. They are harder than platinum, and iridium is alloyed with this metal for special purposes (pen-points and vessels to resist fluorine).

'**Palladium and Platinum.** — Palladium is the only metal of this family which is attacked by nitric acid. Palladium and platinum form *-ous* and *-ic* compounds of the forms PdX_2 and PdX_4, respectively. The oxides PdO and PtO and corresponding hydroxides are basic. When quadrivalent, the metals appear chiefly in complex compounds, like $H_2.PtCl_6$ and $H_2.PdCl_6$, in which the metal is in the anion. Platinum gives also platinates derived from the oxide PtO_2.

Palladium. — This metal (m.-p. 1549°), named from the planetoid Pallas, is noted chiefly for its great tendency to adsorb hydrogen. When finely divided, it takes up about 800 times its own volume, The amount adsorbed varies continuously with

the concentration (pressure) of the hydrogen, although not according to a uniform rule, and the product is in part at least a solid solution. When a strip of palladium is made the cathode of an electrolytic cell, over 900 volumes of hydrogen may be occluded. This adsorbed hydrogen, in consequence of the catalytic influence of the metal, reacts more rapidly than does the gas, and consequently a strip of hydrogenized palladium will quickly precipitate, from solutions of their salts, copper and other metals less electropositive than hydrogen and will reduce ferric and other reducible salts:

$$Cu^{++} + H_2 \rightarrow 2H_{\cdot}^{+} + Cu.$$
$$2Fe^{+++} + H_2 \rightarrow 2Fe^{++} + 2H^+$$
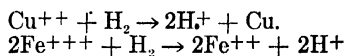
A palladium-gold alloy (palau) has recently been devised as a substitute for platinum in laboratory crucibles.

Platinum.— This metal (Spanish, *plata*, silver) is grayish-white in color, and is very ductile. At a red heat it can be welded. It does not melt in the Bunsen flame, but fuses easily in the oxyhydrogen jet (m.-p. 1755°). On account of its very small chemical activity it is used in electrical apparatus and for making wire, foil, and crucibles and other vessels for use in laboratories. It interacts with fused alkalies, giving platinates. The oxygen acids are without action upon it, but on account of the tendency to form the extremely stable complex ion $PtCl_6^{=}$ (p. 398), the free chlorine and chloride-ion in *aqua regia* convert it into chloroplatinic acid H_2PtCl_6.

The metal condenses oxygen upon its surface and also occludes hydrogen. The finely divided forms of the metal, such as **platinum sponge** made by igniting ammonium chloroplatinate $(NH_4)_2PtCl_6$, **platinum black** made by adding zinc to chloroplatinic acid, and **platinized asbestos** made by dipping asbestos in a solution of chloroplatinic acid and heating it, show this behavior very conspicuously. They cause instant explosion of a mixture of oxygen and hydrogen, in consequence of the heat developed by the rapid union of that part of the gases which is condensed in the metal. A heated spiral of fine platinum wire will continue to glow if immersed in the mixture of methyl alcohol vapor and air (oxygen), formed by placing a little of

the alcohol in the bottom of a beaker. Some cigar-lighters work on this principle. The heat is developed by the interaction between the substances, which takes place with great speed at the surface of the platinum. Specially prepared platinum is used as a contact agent in making sulphur trioxide (p. 336) and in ammonia oxidation (p. 395).

Platinum has approximately the same coefficient of expansion as glass, and it is consequently fused into incandescent bulbs to furnish the electrical connection with the filament in the interior. Large amounts are also consumed in photography and by dentists. The metal is employed most extensively, however, for jewelry.

On account of the increasing demand, and the failure of the Russian supply, platinum is now (1923) worth $108.00 per ounce troy, or more than five times the value of gold (nominally $20.67 per ounce).

Compounds of Platinum. — Platinous chloride is made by passing chlorine over finely divided platinum at 240–250°. It forms with hydrochloric acid the soluble **chloroplatinous acid** H_2PtCl_4. Potassium chloroplatinite K_2PtCl_4 is used in making platinum prints. Bases precipitate black **platinous hydroxide** $Pt(OH)_2$, which interacts with acids but not with bases. Gentle heating gives the **oxide** PtO and stronger heating the metal. With potassium cyanide and barium cyanide soluble **platino-cyanides,** $K_2Pt(CN)_4,3H_2O$ and $BaPt(CN)_4,4H_2O$, are formed.

Chloroplatinic acid $H_2PtCl_6,6H_2O$ is made by treating the metal with *aqua regia*, and forms reddish-brown deliquescent crystals. With potassium and ammonium salts, it yields the sparingly soluble, yellow chloroplatinates K_2PtCl_6 and $(NH_4)_2PtCl_6$ (see pp. 484, 486). **Platinic chloride** $PtCl_4$ is made by heating chloroplatinic acid in a stream of chlorine at 360°. Bases interact with chloroplatinic acid, giving a yellow or brown precipitate of **platinic hydroxide** $Pt(OH)_4$. This substance interacts further with bases to give **platinates,** like $Na_2H_{10}Pt_3O_{12},H_2O$. Both sets of platinum compounds interact with hydrogen sulphide, giving the **sulphides** PtS and PtS_2, respectively.

Exercises. — 1. Make equations for: (a) the action of concentrated sulphuric acid on silver; (b) the decomposition of silver chloride by light.

2. Make equations for: (a) the displacement of gold from potassium chloraurate by silver; (b) the decomposition of chloroplatinic acid, and of (c) ammonium chloroplatinate by heat; (d) the action of zinc on chloroplatinic acid.

3. What would be the advantages and disadvantages of using gold instead of platinum for crucibles?

4. Explain in detail why silver iodide will not dissolve in ammonium hydroxide, why silver bromide goes into solution with some difficulty, and why silver chloride dissolves readily.

5. Justify the nomenclature in the cases of potassium aurocyanide $KAu(CN)_2$ and potassium auricyanide $KAu(CN)_3$ by deducing the valence of gold in each (p. 626).

6. What reagents should you use to precipitate the phosphate, arsenate, and chromate of silver? Write the ionic equations.

7. Write the equations for the interactions of, (a) potassium hydroxide and auric hydroxide, (b) potassium cyanide and sodium chloraurate.

8. In what respects are the elements of this chapter distinctly metallic, and in what respects are they allied to the non-metals (pp. 468-469)?

9. Of which metals should it be possible to obtain colloidal suspensions in water, and of which not (p. 240)? Suggest some liquids in which you should expect to obtain colloidal suspensions of the alkali metals.

CHAPTER XLV

TIN AND LEAD

THE metallic elements of the fifth column of the periodic table are **germanium** (Ge, at. wt. 72.5), **tin** (Sn, at. wt. 118.7), and **lead** (Pb, at. wt. 207.20). These are on the right side, while **titanium** (Ti, at. wt. 48.1), **zirconium** (Zr, at. wt. 90.6), **cerium** (Ce, at. wt. 140.25), and **thorium** (Th, at. wt. 232.15) occupy the left side.

The Chemical Relations of the Family. — All of these elements show a maximum valence of four. Germanium, tin, and lead are also bivalent. In this respect they resemble carbon and differ from silicon, which is more closely allied to the elements on the left side of the column. The oxides and hydroxides in which these three elements are bivalent become more basic, and the elements themselves more metallic in chemical relations, with increase in atomic weight. Curiously enough, the same three hydroxides are also acidic. They are more strongly acidic than is zinc hydroxide, for the salts they form by interaction with bases are less hydrolyzed than are the zincates. This acidic character likewise increases in the order in which the elements are named above.

Germanium and its compounds are not of sufficient importance to delay our progress.

TIN Sn

The Chemical Relations of the Element. — Each of the oxides and hydroxides SnO and $Sn(OH)_2$, SnO_2 and $SnO(OH)_2$ (or $Sn(OH)_4$), is both basic and acidic, so that there are really four series of compounds. Still, stannous hydroxide is mainly a base, of a feeble sort, while stannic hydroxide is mainly an acid. Thus we have stannous chloride, sulphate, and nitrate, which are stable,

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although they are all more or less hydrolyzed by water, and sodium stannite $Na_2.SnO_2$ which is unstable. On the other hand, stannic nitrate, sulphate, and chloride are completely hydrolyzed by water, while sodium stannate Na_2SnO_3 is comparatively stable. The dioxide SnO_2 is an infusible solid, resembling silicon dioxide. Tin has a tendency to give complex acids and salts, like H_2SnCl_6, $(NH_4)_2.SnCl_6$, but these are quite appreciably dissociated in solution, giving ions of Sn^{++++}. Tin forms no salts with weak acids, like carbonic acid.

Occurrence and Extraction. — Tin has long been in use, specimens of it being found in Egyptian tombs. The chief ore of tin is tinstone, or cassiterite SnO_2, which forms square-prismatic crystals whose dark color is due to the presence of iron compounds. The ore is roughly pulverized and washed, to remove granite or slate with which it is mixed, and is then roasted, to oxidize the sulphides of iron and copper, and drive off the arsenic which it contains. After renewed washing to eliminate sulphate of copper and oxide of iron, it is reduced with coal in a reverberatory furnace (p. 695). The tin is afterwards remelted at a gentle heat, and the pure metal which flows away from compounds of iron and arsenic is cast in blocks (**block tin**). Formerly the mines in Cornwall (England) constituted the chief source of the metal, but now the largest supply comes from the East Indies, the next largest from Bolivia. The average total production is 100,000 metric tons annually.

Physical and Chemical Properties. — Tin is a silver-white, crystalline metal of low tenacity but great malleability (tin-foil). Its specific gravity is 7.3, and its melting-point about 232°.

Tin is dimorphous (p. 317). In 1851, the tin pipes of an organ were found to have turned largely into a gray powder. In 1868 a shipment of blocks of tin stored in the custom house in Petrograd was found to have changed in the same way. Objects of tin in museums frequently show spots indicating the presence of the "tin pest," as it was called. It now appears that white, metallic tin is stable only above 18°, and that below this temperature it is unstable and is liable to change into gray tin. This transition point is similar to that of sulphur at 96° (p. 318).

Tin plate, used in making "tin" cans, is produced by dipping cleaned sheets of mild steel in melted tin. So long as the layer of tin remains intact, the iron is protected from rusting. But, if the tin layer is damaged, the tin acts as a contact agent (see p 658) and actually hastens the rusting of the iron.

Tin is sufficiently valuable to render the detinning of scrap tin plate from can factories, bearing 3 to 5 per cent of tin, a paying process. In the Goldschmidt process the scrap is cleaned, dried, and exposed to dry chlorine, which converts the tin into the liquid stannic chloride $SnCl_4$, but leaves the iron unaffected. The chloride is used in mordanting.

Copper vessels for cooking and brass pins are also coated with tin, to preserve them from the action of air and moisture. Tin pipes are used where lead would be unsafe, as, for example, for beverages.

Alloys of tin, such as bronze (p. 604), soft solder (50 per cent lead), pewter (25 per cent lead), and britannia metal (10 per cent antimony and some copper), are much used in the arts.

Tin, although it displaces hydrogen from dilute acids, is not tarnished by moist air. Tin also liberates hydrogen from caustic alkalies, giving a metastannate, such as sodium metastannate Na_2SnO_3.

Chlorides of Tin. — Stannous chloride $SnCl_2,2H_2O$ is made by the interaction of tin and hydrochloric acid. When the crystals are heated, or when a strong aqueous solution is diluted, the salt is partially hydrolyzed. In the latter case the basic chloride $Sn(OH)Cl$ is deposited. By presence of excess of hydrochloric acid, the hydrolysis is prevented. The solution is used as a mordant (p. 591).

Stannous chloride tends to pass into stannic chloride $SnCl_4$, and is therefore an active reducing agent. Thus, it reduces the chlorides of mercury (p. 615) and of the noble metals, liberating the free metals. It also reduces free oxygen, or, what is the same thing, is oxidized by the air. In this case, stannic chloride is formed in the acid solution and the liquid remains clear; in the neutral solution a precipitate of the basic chloride is formed as well:

$$6SnCl_2 + 2H_2O + O_2 \rightarrow 4Sn(OH)Cl + 2SnCl_4.$$
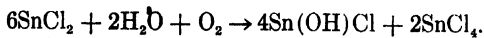
Powdered tin, if placed with the acid solution, will undo the effects of this action by reducing the stannic salt to the stannous condition. ·

When chlorine in excess acts upon tin, **stannic chloride** $SnCl_4$ is formed. The compound is a colorless, liquid (b.-p, 114°) which fumes very strongly in moist air, giving hydrochloric acid and stannic acid. It is almost completely hydrolyzed by water. The stannic acid which is formed is not precipitated, however, but remains in colloidal suspension:

$$SnCl_4 + 4H_2O \rightleftharpoons 4HCl + Sn(OH)_4.$$
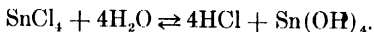
The chloride, with small amounts of water, gives hydrates, of which $SnCl_4,5H_2O$, "oxymuriate of tin," is used as a mordant. Ammonium-stannic chloride or "pink-salt" $(NH_4)_2SnCl_6$ is used· as a mordant on cotton.

α-Stannic Acid and its Salts. — When a solution of stannic chloride is treated with ammonium hydroxide, a white, gelatinous precipitate of α-stannic acid is formed:

$$SnCl_4 + 4NH_4OH \rightarrow 4NH_4Cl + H_2SnO_3 + H_2O.$$ ·

The precipitate loses water gradually until the dioxide remains, and neither $Sn(OH)_4$ nor $SnO(OH)_2$ is obtainable as a definite compound. When stannic oxide is fused with caustic soda, **sodium α-stannate** $Na_2SnO_3,3H_2O$, is formed:

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O.$$
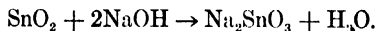
This compound is used as a mordant under the name of "preparing salt." When its solution is acidified, α-stannic acid, the actual mordant, is formed by double decomposition. This α-stannic acid interacts readily with acids and alkalies, and the chloride obtained from it is identical with stannic chloride described above.

· Flannelette and other cotton goods are rendered non-inflammable by saturation first with sodium α-stannate solution and

then, after drying, with ammonium sulphate. The acid is too
feeble to form an ammonium salt:

$$Na_2SnO_3 + (NH_4)_2SO_4 \rightarrow Na_2SO_4 + SnO(OH)_2 + 2NH_3.$$

The sodium sulphate is washed out and the goods, after being
dried, contain stannic oxide. The latter cannot afterwards be
removed by washing, and the material is permanently fireproof.
Silk is also loaded with stannic oxide, the amount used varying
from 25 to 300 per cent or more.

β-**Stannic Acid.** — The first product of the action of concen-
trated nitric acid upon tin is stannic nitrate. Most of this salt,
however, is hydrolyzed by the water at the high temperature of
the action, and there remains a hydrated stannic oxide which is
not identical with the substance described in the foregoing sec-
tion. It is called β-stannic acid, and has been assigned the
formula $(H_2SnO_3)_5$. β-stannic acid is not easily acted upon
by alkalies. By boiling it with caustic soda, however, and then
extracting with pure water, a soluble **sodium β-stannate** $Na_2Sn_5O_{11}$
is obtained. β-stannic acid is also very slowly attacked by acids,
and the chloride secured from it is not identical with the ordinary
chloride. When *fused* with caustic soda, however, β-stannic acid
gives the same α-stannate as does ordinary SnO_2.

The Oxides of Tin. — When stannous oxalate is heated in
absence of air, **stannous oxide** SnO remains: $SnC_2O_4 \rightarrow SnO +$
$CO_2 + CO$. It is a black powder which burns in the air, giving
the dioxide. The corresponding **hydroxide** is formed by adding
sodium carbonate to stannous chloride solution. It is a white
powder, easily dehydrated, and interacts with alkalies to give
soluble stannites, such as Na_2SnO_2. With acids, the hydroxide
gives stannous salts.

Stannic oxide SnO_2 is found in nature (p. 635), and may be
made in pure form by igniting β-stannic acid. When heated, it
becomes yellow, but recovers its whiteness when cooled (compare
zinc oxide, p. 564). Prepared at a low temperature, it interacts
easily with acids, but after strong ignition is affected by them
very slowly.

The Sulphides of Tin. — Stannous sulphide SnS is obtained as a dark-brown precipitate when hydrogen sulphide is led into a solution of a stannous salt.

Stannic sulphide SnS_2 is formed likewise by precipitation, and is yellow in color. Stannic sulphide loses sulphur when strongly heated, and leaves stannous sulphide. It is not much affected by dilute acids, but interacts with solutions of ammonium sulphide (or sodium sulphide), giving a soluble complex salt, **ammonium sulphostannate:**

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2.SnS_3.$$
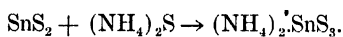
The corresponding **sodium sulphostannate** is easily crystallized in the form $Na_2SnS_3,2H_2O$. Stannous sulphide is not affected by plain sulphides, but polysulphides, such as yellow ammonium sulphide, give with it the above-mentioned sulphostannates:

$$SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2.SnS_3.$$
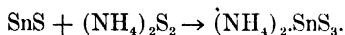
With acids the sulphostannates undergo double decomposition, but the free acid H_2SnS_3 thus produced is unstable and breaks up, giving off hydrogen sulphide, and depositing stannic sulphide.

Analytical Reactions of Salts of Tin. — The two ionic forms of tin, Sn^{++} and Sn^{++++}, are both colorless. Their behavior is different. They give a brown and a yellow sulphide, respectively, with hydrogen sulphide. These sulphides dissolve in yellow ammonium sulphide. The reducing power of stannous-ion Sn^{++} is very characteristic (p. 615). The oxides are reduced by charcoal in the reducing part of the Bunsen flame and the metal is liberated.

LEAD Pb

The Chemical Relations of the Element. — The oxides PbO and PbO_2, and the corresponding hydrated oxides, are all both basic and acidic. Lead monoxide is a fairly active base, comparable with cupric oxide, but lead dioxide is a feeble one. Both are feebly acidic. The salts of bivalent lead, like $Pb(NO_3)_2$, are somewhat hydrolyzed by water, but less so than are those of

tin. The tetrachloride and other salts of quadrivalent lead are completely hydrolyzed. The plumbites $Na_2.PbO_2$ and plumbates $Na_2.PbO_3$, like the stannites and stannates, are hydrolyzed to a considerable extent. All the compounds in which lead is quadrivalent are readily reduced. The metal displaces hydrogen with difficulty (see table on p. 240), and is easily displaced by zinc. Lead compounds are all poisonous.

Occurrence and Metallurgy. — Commercial lead is almost all obtained from galena PbS, which crystallizes in cubes, and is found in the United States, Spain, and Mexico.

The ore, if rich, is roasted in a reverberatory furnace (p. 695) until a part has been converted into the oxide PbO and sulphate $PbSO_4$. The air is then shut off, and the temperature raised, so that these products may oxidize the remaining galenite:

$$PbS + 2PbO \rightarrow 3Pb + SO_2 \uparrow$$
$$PbS + PbSO_4 \rightarrow 2Pb + 2SO_2 \uparrow .$$
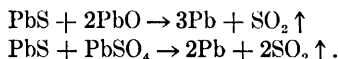
The melted lead flows out.

Ores poorer in lead are sometimes reduced by heating with scrap iron, or with a mixture of iron ore and coke.

Lead is refined electrolytically by the **Betts process.** Heavy plates of the crude lead form the anodes, thin sheets of pure lead the cathodes, and a solution of lead fluosilicate $PbSiF_6$ the cell liquid. The operation is similar to that for refining copper (p. 613). Silver, gold and bismuth are left as a sludge.

Physical and Chemical Properties. — Metallic lead is gray in color, very soft, and of small tensile strength. Its specific gravity is 11.4, and its melting-point 327.4°. While warm, it is formed by hydraulic pressure into pipes which are used in plumbing and for covering electric cables. On account of its very slow interaction with most substances, sheet lead is used in chemical factories, for example, to line sulphuric-acid chambers. An alloy containing 0.5 per cent of arsenic is used in making small shot and shrapnel bullets. Type-metal contains 20–25 per cent of antimony and expands on solidifying, giving a perfect reproduction of the mold. In both cases greater hardness is

secured by the addition of the foreign metal. Solder contains 50 per cent of tin and, since it remains liquid at a lower temperature than pure lead, can be applied in the molten state to mend a lead joint without danger of melting the lead itself.

Lead oxidizes very superficially in the air. The suboxide Pb_2O is supposed to be first formed. The final covering is a basic carbonate. Contact with hard waters confers upon lead a similar coating composed of the carbonate and the sulphate. These deposits, being insoluble and strongly adherent, enclose the metal and protect the water from contamination with lead compounds. Pure rain-water, however, since it has no hardness, and contains oxygen in solution, gives the hydroxide $Pb(OH)_2$, which is noticeably soluble. Hence lead pipes can safely be used only with somewhat hard water. When heated in the air, lead gives the monoxide PbO or minium Pb_3O_4, the latter at lower temperatures.

The metal displaces hydrogen from hydrochloric acid slowly. It is hardly affected by cold concentrated sulphuric acid (compare p. 344). Nitric acid attacks it readily, giving lead nitrate and oxides of nitrogen (p. 397).

The annual world's production of lead averages 1,000,000 tons. It is the cheapest metal after iron. Its principal uses have been described above. The metal is also employed extensively in **storage batteries** (see p. 660). Its compounds find important applications as **paint ingredients** (p. 644).

Chlorides and Iodide.—— Lead chloride $PbCl_2$ is precipitated when a soluble chloride is added to a solution of a bivalent lead salt. It is slightly soluble in water (1.5 parts in 100) at 18°, and much more so at 100°.

Lead tetrachloride $PbCl_4$ is a solid at $-15°$, and loses chlorine at the ordinary temperature. It is made by passing chlorine into $PbCl_2$ suspended in hydrochloric acid. The solution contains the complex acid H_2PbCl_6. Ammonium chloride is added and ammonium chloroplumbate $(NH_4)_2PbCl_6$ crystallizes out. When this is thrown into cold, concentrated sulphuric acid, an oil, $PbCl_4$, settles to the bottom. The oil fumes in the air, and closely resembles stannic chloride $SnCl_4$. With little water, it

.slowly deposits $PbCl_2$ and gives off chlorine. With much water it is quickly hydrolyzed, and lead dioxide is thrown down:

$$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl.$$
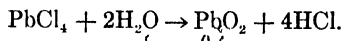
The yellow **lead iodide** PbI_2 is formed by precipitation. It crystallizes in yellow scales from solution in hot water.

Oxides and Hydroxides. — There are five different oxides of lead, Pb_2O, PbO, Pb_3O_4, Pb_2O_3, and PbO_2. The **suboxide** Pb_2O is a dark-gray powder, formed by gently heating the oxalate. Lead 'monoxide PbO is made by cupellation (p. 621) of lead, and the solidified, crystalline mass of yellowish-red color is sold as **litharge.** All the other oxides yield this one when they are heated above 600° in the air. It is used in making glass and enamels and for preparing salts of lead. Mixed with glycerine, it gives a cement for glass or stone.

The **hydroxide** $Pb(OH)_2$ is formed by precipitation. It is observably soluble in water, and gives a solution with a faintly alkaline reaction. With acids it forms salts of lead. It interacts also with potassium and sodium hydroxides to form the soluble **plumbites,** like **sodium plumbite** $Na_2.PbO_2.$

Minium, or **red lead,** Pb_3O_4, gives off oxygen when heated:

$$2Pb_3O_4 \rightleftarrows 6PbO + O_2.$$
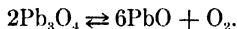
'On account of unequal heating during manufacture, commercial red lead is never fully oxidized, and always contains litharge. Conversely, commercial litharge usually contains a little minium.

Minium, when heated with warm, dilute nitric acid, is decomposed, and leaves lead dioxide as an insoluble powder. Two-thirds of the lead is basic and one-third is acidic. Minium is therefore lead orthoplumbate (see below):

$$Pb_2.PbO_4 + 4HNO_3 \rightleftarrows 2Pb(NO_3)_2 + H_4PbO_4.$$
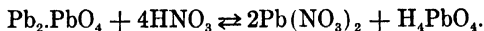
The double decomposition as a salt that it thus undergoes is followed by dehydration of the plumbic acid, which is unstable $(H_4PbO_4 \rightarrow PbO_2 + 2H_2O)$, and the dioxide remains. Red lead is used in glass-making, and, when mixed with oil, gives a red paint.

Lead dioxide PbO_2 may be obtained as described above in the form of a brown powder. It is usually made by adding bleaching powder to an alkaline solution of $Pb(OH)_2$:

$$Na_2.PbO_2 + Ca(OCl)Cl + H_2O \rightarrow 2NaOH + CaCl_2 + PbO_2 \downarrow.$$
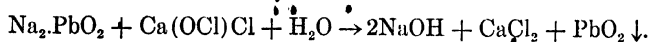
In this action we may regard the free lead hydroxide, formed by hydrolysis of the plumbite, as being oxidized by the bleaching powder. Lead dioxide is an active oxidizing agent. It interacts with, and sets fire to, a stream of hydrogen sulphide, and it liberates chlorine from hydrochloric acid. With acids it gives no hydrogen peroxide, and its graphic formula $O = Pb = O$ indicates that it is **not** a peroxide (p. 292). Lead dioxide interacts with potassium and sodium hydroxides, giving soluble **plumbates.** The potassium salt $K_2PbO_3,3H_2O$ is analogous to the metastannate $K_2SnO_3,3H_2O$ (p. 637). A mixture of calcium carbonate and lead monoxide absorbs oxygen when heated in a stream of air, and the yellowish-red calcium orthoplumbate is formed:

$$4CaCO_3 + 2PbO + O_2 \rightleftarrows 2Ca_2PbO_4 + 4CO_2.$$
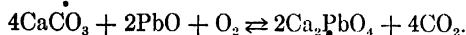
The action is reversible, and is at the basis of Kassner's method of manufacturing oxygen from the air.

Other Salts of Lead. — Lead carbonate $PbCO_3$ is found in nature. It may be formed as a precipitate by adding sodium bicarbonate to lead nitrate solution. With normal sodium carbonate, a basic carbonate $Pb_3(OH)_2(CO_3)_2$ is deposited. This basic salt is identical with **white lead,** a heavy, white, insoluble, amorphous substance. Mixed with linseed oil, it forms a white paint valued for its "body" or covering power (see Paints, p. 644). Its disadvantage is the darkening, due to formation of the black lead sulphide PbS, which is produced by the hydrogen sulphide in the air (see p. 293). Its poisonous character is also objectionable.

The old **Dutch process** for making white lead is still used extensively. Gratings ("buckles") of lead are placed above a little vinegar in small pots. The pots are covered with boards, on which manure or spent tan bark is spread. Other tiers of pots, boards and bark are placed on the first, until the shed is full. Carbon dioxide, warmth and moisture are furnished by the

decaying bark. The gratings, by the end of three months, are converted into cakes of white lead. The vapor of acetic acid arising from the vinegar may be regarded as a catalytic agent.

In **Mild's process** melted lead is atomized by a jet of steam, and the lead dust is beaten with vinegar, air, and carbon dioxide in a vat for about seven days. In the **French process** white lead is precipitated by a stream of carbon dioxide from a *solution* of the basic acetate.

Lead acetate $Pb(C_2H_3O_2)_2,3H_2O$ is made by the action of acetic acid on litharge. It is easily soluble in water and, from the sweet taste of the solution, is named **sugar of lead** (used in medicine).

Lead sulphate $PbSO_4$ occurs in nature as anglesite. It is a very insoluble salt. On this account, the workmen in white lead works add a little sulphuric acid to the water they drink.

Paints. — A paint usually contains three ingredients: 1. The **oil**, which hardens ("dries") to a tough resin, being oxidized by the air, and adheres firmly to the surface being painted.

2. The **body**, a fine powder which makes the paint opaque. Since the powder does not shrink, it also "fills" the paint and prevents the formation of minute pores which otherwise would appear in the oil after drying. White lead is the most common material for the body, but zinc oxide and other substances are also used.

3. Except in the case of white paint, a **pigment** is added. Various oxides, such as minium, colored salts, and lakes (p. 592) are used as coloring matters.

The oil does not "dry" by evaporation but gives a resin by oxidation (see p. 42). Linseed oil and hemp oil are commonly used. They contain glyceryl esters (p. 545) of unsaturated acids, such as that of linoleic acid, $(C_3H_5(CO_2C_{17}H_{31})_3)$. The unsaturated part of the molecule takes up the oxygen. By previously boiling the oil with manganese dioxide and other oxides, it is rendered more active, and "dries" more quickly.

Plumbers use a cement made of minium and linseed oil, in which the former oxidizes the latter, without access of air being necessary, to make joints tight.

Analytical Reactions of Lead Compounds. — Hydrogen sulphide precipitates the black sulphide, even when dilute acids are present. Sulphuric acid throws down the sulphate. Potassium hydroxide gives the white hydroxide, which dissolves in excess to form the plumbite. Potassium chromate or dichromate (p. 679) gives a yellow precipitate of lead chromate $PbCrO_4$, which is used as a pigment under the name of "chrome-yellow."

TITANIUM, ZIRCONIUM, CERIUM, THORIUM

The metals on the left side of the fifth column of the periodic table are all quadrivalent, although compounds in which a lower valence appears are numerous in this family. The first two are feebly base-forming as well as feebly acid-forming; the last two are base-forming exclusively.

Titanium occurs in rutile TiO_2. **Zirconium** is found in zircon, the orthosilicate of zirconium $ZrSiO_4$ (see Fig. 45, p. 105).

Cerium occurs chiefly in cerite, a complex silicate in which neodymium, praseodymium and lanthanum (p. 580) are also present. The particles of an alloy of cerium (70 per cent) and iron (30 per cent), when torn off by a file, catch fire in the air. This fact is utilized in making **gas-lighters** and cigar-lighters. **Thorium** is found in thorite $ThSiO_4$, but most of the supply comes from monazite sand. The nitrate $Th(NO_3)_4,6H_2O$ is used in making Welsbach incandescent mantles (compare p. 443). The element and its compounds are radioactive (see p. 723).

The foundation of the **Welsbach mantle** is woven of ramie. This is saturated with a solution of thorium and cerium nitrates in the proportion 99 : 1, and is then molded to the proper shape and dried. By heating in a Bunsen flame, the organic matter is burned, and the nitrates are decomposed:

$$Th(NO_3)_4 \rightarrow ThO_2 + 4NO_2 + O_2.$$
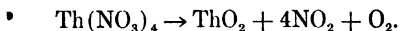
The oxides retain the form of the fabric and, to prevent breakage in handling, the structure is dipped in collodion and dried.

Exercises. — 1. In what order should you place the elements dealt with in this chapter, beginning with the least metallic, and ending with the most metallic (pp. 468-469)?

2. Construct equations showing, (a) the interaction of tin and concentrated sulphuric acid, (b) of water and stannous chloride, (c) of oxygen and stannous chloride in acid solution, (d) of lead monoxide and acetic acid.

3. Formulate ionic equations to explain why stannic sulphide dissolves in ammonium sulphide solution.

4. What interactions probably occur when lead dioxide liberates chlorine from hydrochloric acid (see p. 178)?

5. How should you set about preparing, (a) lead oxalate (insoluble), (b) lead chlorate (soluble)?

6. Construct equations for the formation of white lead by the Dutch process, showing, (1) the formation of the basic acetate by the action of oxygen, water, and acetic acid vapor, and (2) the action of carbonic acid on the product.

CHAPTER XLVI

ELECTROMOTIVE CHEMISTRY

IN chemical changes involving electrolytes, which liberate energy, the energy can be secured, if special arrangements are made, in the form of electricity. Since the change sets an electric current in motion, the subject is called **electromotive chemistry.** A knowledge of this branch of the science is essential for the proper understanding of many commercial applications of electricity in chemistry, such as electrolytic methods of refining metals, the theory of storage batteries, etc. It also furnishes us with a simple method for measuring chemical affinity in ionic reactions.

Factors and Units of Electrical Energy. — On account of the close relation between electromotive chemistry and ionization, parts of the former subject were anticipated when the latter was discussed (pp. 235-240). These pages should now be re-read attentively. In particular, it must be recalled that **a quantity of electrical energy is expressed by two factors.** One is called the **quantity of electricity,** and is measured in **coulombs.** The other is called the **electromotive force** in the case of a current, or, when a current is not flowing or is not being considered, the **difference in potential,** and is expressed in **volts.** Just as in electrolysis chemically equivalent quantities of elements or ions, in being liberated from solutions of different substances, *use up* equal quantities of electricity (Faraday's law), so in a battery-cell the interaction of chemically equivalent amounts of different sets of substances *produces* equal quantities of electricity. On the other hand, just as different amounts of thermal energy are liberated or absorbed by different chemical reactions (p. 200), so different amounts of electrical energy are used or generated by the complete interaction of chemical equivalents of different

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sets of substances, and therefore diverse differences in potential are created and **currents of different electromotive force** are produced. The electrical energy used or produced is expressed by the product of the factors:

No. of coulombs $\times$ No. of volts
    $=$ Quantity of electrical energy (in **joules**).

If we consider the time occupied by either process, and wish to express the **rate** at which the energy is consumed or produced, we regard 1 coulomb per second (1 **ampere**) as the unit. Hence:

No. of amperes $\times$ No. of volts $=$ Joules per sec. $=$ **Watts.**

The kilowatt is 1000 watts. The horsepower is 746 watts.

An illustration will show the meaning of this relation. If a 50-watt incandescent lamp is used on a 110-volt circuit, by substituting these values in the equation we perceive that such a lamp must carry about 0.5 amperes, or one coulomb every two seconds. If, with the *same* voltage, we wanted a lamp to carry more electricity per second, we should have to reduce the resistance of the lamp, say, by shortening the filament, or using a thicker one. Evidently, the number of such lamps required to consume one horsepower would be 746/50, or between 14 and 15 lamps. Again, to decompose one molecular weight of hydrochloric acid (36.468 g.) 96,540 coulombs (p. 237) are required, and an E.M.F. of at least 1.35 volts (see p. 657). The electrical energy needed is therefore $96,540 \times 1.35 = 130,300$ joules. If this were to be accomplished by the current from a 110-volt direct-current lighting circuit, passing through a lamp which carried 5 watts when in series with the electrolytic cell, the time required (x seconds) would be given by: 5 joules per sec. $\times$ x secs. $= 130,300$ joules, where $x = 26,060$ seconds, or about $7\frac{1}{4}$ hours.

The factors of electrical energy (volts and amperes) are easily measured when electricity is produced, and are easily provided according to any specification when electricity is to be used. Hence, it is much easier to study the relations between chemical change and this form of energy than between the same change

and the heat or any other form of energy which, under other conditions, it might produce. Electrochemistry is, therefore, in many ways better understood, and easier to handle than are other branches of chemistry involving energy.

Some Reactions that can be Used to Furnish Electricity. — A few illustrations of the kinds of reactions which can easily be carried out in cells, so as to furnish an electric current instead of heat, may be classified thus:

Combination cells, such as one in which zinc (or some other active metal) and bromine (or some other active non-metal) are the reacting substances:

$$Zn^0 + Br_2^0 \rightarrow Zn^{+.+} + 2Br^-$$
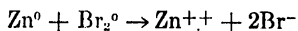
Displacement cells, such as one with cupric sulphate solution and a metal more active than copper (p. 240):

$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0.$$
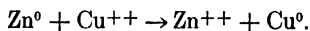
Oxidation cells, such as one in which ferrous chloride $FeCl_2$ or stannous chloride $SnCl_2$ is oxidized by chlorine-water, giving $FeCl_3$ or $SnCl_4$:

$$Sn^{++} + Cl_2^0 \rightarrow Sn^{++++} + 2Cl^-.$$

Concentration cells, or cells in which the same substance, such as silver nitrate, in two different concentrations is used.

On closer analysis, as we shall see below, all of these reactions reduce to the same type — **oxidation** (or **loss of electrons,** see pp. 267, 300) at one electrode, and **reduction** (or **gain of electrons**) at the other.

The Arrangement of the Cell. — Every cell has one striking characteristic. If the pairs of substances mentioned in the last section are *placed together,* they interact and *heat* is produced. There is no way to avoid the action, and the liberation of the energy as heat, if the substances come in contact. If, therefore, **all the energy is to be obtained as electrical energy, the substances must be prevented from coming in contact with one another.** Paradoxical as it may seem, it is easily possible to obtain the

electricity, and yet fulfill this essential condition. The plan in all cells is to place the one substance in or round one pole, and the other substance in or round the other pole, and to separate the substances by a porous partition, or some equivalent arrangement.

Suppose that it is the first of the above-mentioned actions that is to be used — the action of zinc and bromine. The **active substances are arranged** as follows: The pole on the left (Fig. 130)
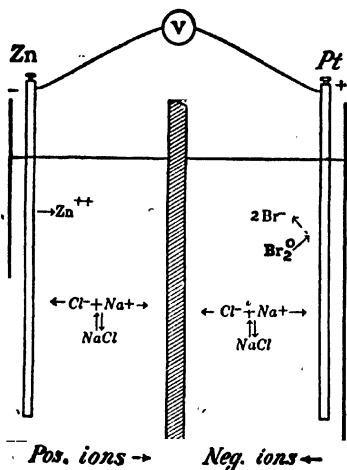
Fig. 130.

is metallic zinc. The solution on the right contains the bromine. The porous partition in the center is permeable by migrating ions, but hinders mechanical mixing of the materials in the two halves of the apparatus, and so prevents direct interaction with liberation of heat.

Now, to enable the cell to operate, **inactive, conducting substances must be added** to complete the arrangement. A pole is added on the right, a conducting solution is placed to the left of the partition, and a wire must connect the two poles. The wire may connect the poles through a voltmeter, so that the E.M.F. produced may be measured. Also, since bromine-water is a poor conductor, a well-ionized salt must be present along with the bromine. The substances used for these purposes must be inactive. For example, the pole on the right must be a conductor, but its material must not interact chemically with the bromine or with the salt. A rod of carbon or a platinum wire will serve the purpose. A more active metal, such as copper, could not be used, because it would combine with the bromine. Again, common salt or sodium nitrate may be mixed with the bromine, because it will not interact with bromine or carbon or platinum. Still again, the solution added on the left

must be one which will not act upon the zinc pole, or upon the solution on the right, which it meets inside the porous partition. Common salt or niter fulfills these conditions. An acid could be used on the right, but not on the left, for it would interact with the zinc. The reader should make a different selection of inactive materials, so as to become familiar with the reasoning involved in the choice in each case.

Note that in each figure, the symbols for the **active substances** are in **black-face** type, the products are in Roman type, and the *inactive* materials are in *italic* type.

The Operation of the Cell. — When the cell has been assembled, and the wires have been connected, the following phenomena are observed:

1. The zinc, in consequence of its tendency to lose electrons (p. 267), begins to form zinc ions, $Zn^0 \to Zn^{++} + 2\ominus$, an operation which leaves the pole negative.

2. The bromine molecules which come into collision with the other pole, in consequence of their tendency to gain electrons (p. 284), begin to form bromide ions, $Br_2^0 + 2\ominus \to 2Br^-$, and leave this pole positively charged.

3. Since one pole is now negative and the other positive, a current flows through the wire.

4. The new positive ions (Zn^{++}) round the left pole (anode) attract *all* the negative ions in the cell, and cause them to migrate towards the left so as to keep all parts of the solution electrically neutral.

5. The new negative ions on the right (Br^-) similarly attract *all* the positive ions in the cell, and cause them to drift slowly towards the right pole (cathode).

6. (Very important.) It will be seen that the zinc and the bromine **become ionized at a distance from one another and do not actually combine.** The slow migration of the Zn^{++} and Br^- ions will, of course, after some hours or days, bring some of these ions together in or near the partition, and some undissociated $ZnBr_2$ will be formed. But this operation produces no electrical energy — it only gives out or absorbs heat (p. 195). It is not an essential part of the operation of the cell. **The chemical change which**

produces the current is the ionization of the two elements, separately. The term combination cell is, therefore, misleading. The cell, as a source of electrical energy, is concerned only with producing two kinds of ions from the elements:

$$Zn^0 + Br_2{}^0 \rightarrow Zn^{++} + 2Br^- + \text{Electrical energy.}$$
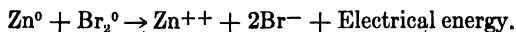
A Displacement Cell. — In a similar way, a cell using metallic zinc and cupric sulphate solution may be arranged (Fig. 131). The zinc forms one pole, and the cupric sulphate solution *must be placed on the other side* of the partition. For inactive materials, a plate of copper or of some metal below copper in the activity series may be used, and any solution (such as zinc chloride solution) which will interact neither with the zinc nor with the cupric sulphate.
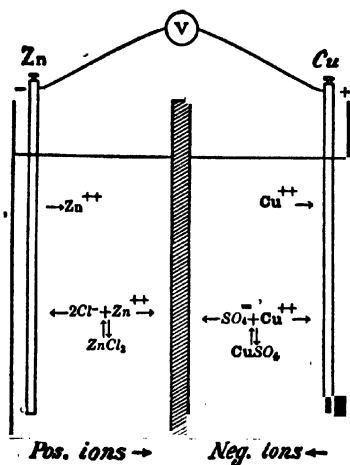
Fig. 131.

The operation of the cell is substantially as in the previous example. Thus, the zinc begins to lose electrons and gives zinc ion $Zn^0 \rightarrow Zn^{++} + 2\ominus$. The pole on the left becomes negatively charged. The cupric ions which collide with the pole on the right tend to discharge, and consequently begin to gain electrons $Cu^{++} + 2\ominus \rightarrow Cu^0$, leaving the pole positively charged. All the positive ions in the cell migrate towards the right pole (cathode) and all the negative ions migrate towards the left pole (anode), since positive ions are being formed on the left and are disappearing on the right:

$$Zn^0 + Cu^{++} \rightarrow Zn^{++} + Cu^0 + \text{Electrical energy.}$$
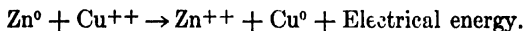
The Oxidation Cell. — The arrangement whereby stannous-ion Sn^{++} is oxidized by chlorine-water to stannic-ion Sn^{++++}

is shown in Fig. 132. ' The chlorine Cl_2^0 encountering the pole on the right' gains electrons and becomes negatively charged, leaving the pole positive. Transfer of electrons takes place along the whole conducting wire (see p. 468). The source of these electrons is the reaction which takes place when stannous ions Sn^{++} touch the electrode on the left: $Sn^{++} \rightarrow Sn^{++++} + 2\ominus$. The complete reaction is therefore:

$$Sn^{++} + Cl_2^0 \rightarrow Sn^{++++} + 2Cl^- + \text{Electrical energy.}$$
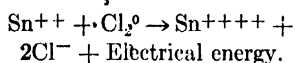
A rather more complex example of an oxidation cell is obtained when we introduce hydrochloric acid on the one

Pos. ions $\rightarrow$ Neg. ions $\leftarrow$

FIG. 132.

side of our apparatus and a solution of potassium permanganate on the other. The reaction which occurs in this case:

$$2MnO_4^- + 16H^+ + 10Cl^- \rightarrow 2Mn^{++} + 8H_2O + 5Cl_2^0$$
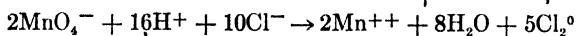
may thus also be utilized as a source of electrical energy. The student should refer back, at this point, to the detailed discussion given to this reaction in an earlier chapter (pp. 303-305).

Facts Concerning All Cells. — If the wire is disconnected, the progress of the oxidation and reduction reactions at the respective electrodes automatically stops. The charge conferred upon a pole must be conducted away, before additional charges will be transferred to it.

If a glass partition is substituted for a porous one, the cell ceases to generate electricity. The partition must permit the trans-migration of the ions, which is a necessary part of the operation of the cell.
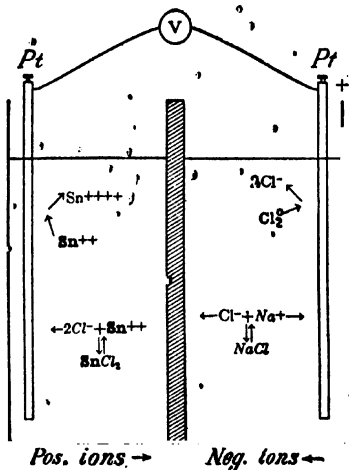
When the circuit is closed, the changes described go on until one of the active materials is practically exhausted — for example, until practically all the cupric-ion has been deposited as copper, or until practically all the zinc has been consumed.

The quantity of electricity produced is 96,540 coulombs for each equivalent weight of the active materials transformed, *e.g.*, for every 65.37/2 g. of zinc consumed. The *rate* at which the electricity is produced is, in general, greater the larger the area of the poles. The amperage of a *single* cell is, in general, very low.

The E.M.F. of the cell is not changed by altering the size or shape of the poles, or by using more or less of the solutions. It *is* affected by any change in the *qualities* of the *active* materials, however. Changing the concentration of the cupric-ion (Fig. 131) or of the bromine-water (Fig. 130) has an immediate effect. So has substituting one active metal for another, as magnesium for zinc (Fig. 130). The reasons for such differences may now be developed.

Single Potential Differences Produced by the Metals. — It will be evident, from the discussion on the operation of the cells given above, that there are really **two chemical actions in each cell** and that these are to some extent independent. We can leave the zinc (Fig. 130) constant, and change the concentration of the bromine or even substitute chlorine or iodine for the latter. The reaction: $Zn^0 \rightarrow Zn^{++} + 2\ominus$ at the negative pole is unaffected. On the other hand, we can leave the bromine-water constant, and exchange the zinc for some other active metal, without disturbing the reaction: $Br_2^0 + 2\ominus \rightarrow 2Br^-$ at the positive pole. Thus, the E.M.F. of every cell is really the resultant of two effects. Now these effects can be considered separately.

If we place zinc in a solution of zinc chloride, we find that there is at once a difference in potential between the metal and the solution. The atoms of the metal have an individual tendency to assume the ionic state or, in other words, to give up electrons (p. 267): $Zn^0 \rightarrow Zn^{++} + 2\ominus$. On the other hand, the Zn^{++} ions already in the solution have a tendency to take up electrons and become neutral, according to the reverse equation:

$Zn^{++} + 2\ominus \rightarrow Zn^0$. If the former tendency (the tendency to give up electrons) is the stronger of the two (as it is, for solutions of ordinary concentration, with the more active, metals), then a difference in potential is produced, with the solution positive with respect to the metal. If the latter tendency is the stronger (as it is, for solutions of ordinary concentration, with the less active metals) the solution is observed to be negative with respect to the metal. Raising the concentration of the metal-ions will increase the tendency to deposition and *vice versa*, while the tendency of the metal to form metal-ions is constant (compare, very carefully, the discussion on solution equilibria, p. 156). It is customary, therefore, always to take as the standard solution, in comparing potential differences, one in which the concentration of the metal-ions is normal (N). It is also customary, in consequence of the impossibility of determining absolute electrode potentials accurately, to assume the potential of a platinum electrode saturated with hydrogen gas under 1 atmosphere pressure against a solution normal with respect to hydrogen-ion as zero, and to refer all other potentials to this as a standard. This does not mean that the reaction: H_2 (at 1 atm.) $\rightarrow 2H^+$ (in N solution) $+ 2\ominus$ involves no gain or loss of electrical energy, but only that the potentials of other elements against normal concentrations of their ions differ from that of hydrogen by the values given. In the following table, the sign preceding the number is the charge of the free metal. It will be seen that the most *electropositive* metals acquire the highest *negative* potential, in consequence of their extreme tendency to throw off *positively charged ions:* $K \rightarrow K^+ + \ominus$.

POTENTIALS OF METALS IN CONTACT WITH N SOLUTIONS
(ELECTROMOTIVE SERIES)

Li	−3.02	Cr (Cr++)	−0.6(?)	Sb	+0.1(?)
K	−2.92	Cr (Cr+++)	−0.5(?)	Bi	+0.2(?)
Na	−2.72	Fe (Fe++)	−0.43	As	+0.3(?)
Ba	−2.8(?)	Cd	−0.40	Cu (Cu++)	+0.34
Ca	−2.5(?)	Ni (Ni++)	−0.22	Cu (Cu+)	+0.51
Mg	−1.55	Sn (Sn++)	−0.14	Hg (Hg+)	+0.79
Al	−1.34	Pb (Pb++)	−0.13	Ag	+0.80
Mn (Mn++)	−1.0(?)	Fe (Fe+++)	−0.04	Hg (Hg++)	+0.86
Zn	−0.76	H₂	0.00	Au (Au+)	+1.5(?)

The "normal potentials" of some non-metallic ,elements, and of some typical oxidation-reduction reactions, may also be appended:

F₂	$+ 1.9(?)$	$O_2 + 2H_2O + 4\ominus \rightarrow 4OH^-$	$+ 0.40$
Cl₂	$+ 1.35$	$MnO_4^- + 8H^+ + 5\ominus \rightarrow Mn^{++} + 4H_2O$	$+ 1.52$
Br₂	$+ 1.08$	$Pb + SO_4^= \rightarrow PbSO_4 + 2\ominus$	$- 0.34$
I₂	$+ .0.62$	$PbO_2 + 2H^+ + 2\ominus \rightarrow H_2O + PbO$	$+ 1.66$

Applications: E.M.F. of a Displacement Cell. — For a cell in which one metal is going into solution and another is being

deposited — like that with zinc and cupric sulphate — we can calculate from the foregoing data the E.M.F. of the cell. Metallic zinc, in contact with normal zinc-ion solution, acquires a *negative* potential of 0.76 volts. Metallic copper, in contact with normal cupric-ion solution, acquires a *positive* potential of 0.34 volts. The potential difference between the two electrodes is con-

FIG. 133.   sequently the difference of these values, *i.e.*, 1.10 volts, and this will represent the E.M.F. of a cell such as is given in Fig. 131 when the concentrations of the metal-ions on the two sides are normal.
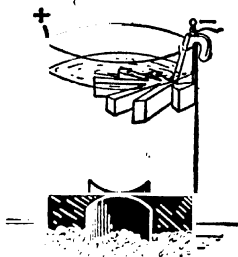
The Daniell or gravity cell (Fig. 133) makes use of the above facts. The copper plate is at the bottom and the zinc is suspended above it. The cell is filled with dilute sodium chloride solution and crystals of cupric sulphate are thrown in. So long as the cell is not disturbed, the heavy, saturated solution of cupric sulphate remains at the bottom, so that no porous partition is required. The actual E.M.F. of this cell is not exactly that calculated for normal solutions, because the cupric sulphate is in saturated solution, and the concentration of the zinc-ion varies, starting at zero and increasing as the cell is used. It is, however, a little over 1 volt.

The **Weston Standard Cell** contains a pole of mercury in a saturated solution of mercurous sulphate and cadmium in contact with saturated cadmium sulphate solution. For normal ionic concentrations, the voltage of such a combination would be

$0.79 + 0.40 = 1.19$ volts. At 20° the Weston cell, as actually set up, possesses 1.0183 volts.

The **Clark Standard Cell** contains zinc and zinc sulphate solution in place of the cadmium. With normal ionic concentrations this combination would give $0.79 + 0.76 = 1.55$ volts. With saturated solutions, as used in practice, it gives 1.434 volts.

Electrolysis: Decomposition Potentials. — When a solution of cupric chloride is electrolyzed, copper and chlorine are liberated at the two poles. Now, when the electrolysis has made some progress, if the battery is taken out, and the wires are joined, a current, the **polarization current**, flows. Evidently, the copper and chlorine liberated in and round the electrodes have made the arrangement into a copper-chlorine battery cell. Assuming normal ionic concentrations, the E.M.F. of the polarization current is $1.35 - 0.34 = 1.01$ volts. Now this counter-current is in operation during the whole electrolysis. To overcome it, and maintain the electrolysis, evidently an E.M.F. of at least 1.01 volts from the battery is required. This is called the **decomposition potential** for cupric chloride. The decomposition potentials of other electrolytes in solutions of normal ionic concentration may be calculated by the student from the tables given above.

Electrolytic Refining. — The electrolytic process for refining copper (read p. 613) can now be more easily understood. *Both* electrodes are made of copper, and the solution contains cupric sulphate. There is, therefore, no difference in potential between the plates, except a very small one, due to the fact that one plate is pure copper and the other impure. Hence a very slight E.M.F., sufficient to overcome the difference just mentioned, and to move the ions at a suitable speed between the electrodes (see p. 242), is all that is required, and with a high amperage less than 0.5 volts is sufficient.

As regards the resulting **purification**, the anode of crude copper, which is being consumed, contains, besides copper, small amounts of less active metals like silver and gold, and of more active metals like zinc. So far as the more active metals are concerned, the cell is like one with zinc and cupric sulphate

(p. 652). It would run *by itself*, without any outside current, and would actually generate a current. Hence the active metals easily become ionic, and displace cupric-ion from the solution. The less active metals, on the other hand, require a larger E.M.F. for their ionization than is being supplied. Hence they remain as metals, and drop to the bottom of the cell (sludge) as the anode of crude copper wears away.

Couples. —We have noted (pp. 63, 195) that contact with a platinum wire, or the presence of impurities (other metals) in zinc, will hasten its action upon an acid. Pieces of two metals in contact with one another constitute a **couple**. With zinc and platinum in an' acid, a current is set up, like that of a short circuited cell. The zinc becomes negative, the platinum positive, and the hydrogen is *liberated upon the platinum*. This facilitates the action because, when the platinum is absent, and the hydrogen gas, in bubbles, is liberated on the surface of the zinc, this surface is only partly in contact with the acid (H^+), and so the liberation of the hydrogen is slower.

Galvanized iron is also a couple. When rain (dilute carbonic acid) falls upon it, the zinc, being the more active metal (p. 563), is the anode and tends to become ionized (forming the carbonate). The iron is the cathode and is not affected. The carbonate, however, forms a closely adhering coating on the zinc, and so but little of this metal is actually consumed, and the material is therefore durable. On the other hand, a sheet of iron, without the zinc coating, gives ferrous carbonate which is easily oxidized to ferric hydroxide (a base too weak to give a carbonate). This forms a brittle, porous layer which does not mechanically protect the surface from further action, and so the iron is finally all oxidized. **Tin-plate** (tin on iron, a couple) is not attacked so long as the layer of tin is nowhere broken. But damaged tin-plate rusts rapidly. There, the iron is the more active metal (p. 636) and forms carbonate and then hydroxide continuously, while the tin remains unaffected.

Measurement of Affinity. — Since equal quantities of electricity bring about (or are brought about by) chemical changes in chemically equivalent weights of material, it follows that the

electromotive forces required (or produced) are proportional to
the chemical' affinity. Thus the activities of the metals, ex-
pressed in volts (p. 655), are accurate figures for the relative
affinities of the metals, so far at least as ionic actions are con-
cerned. In point of fact, they express also the approximate
affinities of the metals in other actions (pp. 65, 180) as well
Again, by using different oxidizing agents in place of the chlorine-
water (p. 653) and noting the differences in potential, we can
obtain numbers representing the relative activities of various
oxidizing agents towards oxidizable ions.

Concentration Cells. — If two rods of a metal (*e.g.*, silver)
are placed together in the same solution of a salt of the metal
(*e.g.*, silver nitrate AgNO₃), there is no difference in potential,
because the state of both poles is in all respects the same. But
if the solution round one pole is more concentrated than that
round the other, a difference in potential is produced (Fig. 134).
The tendencies of the metallic silver to form ions are equal, but
the tendencies of the silver
ions to deposit upon the elec-
trodes are different (see p.
655, and so when the circuit
is closed, silver ions are dis-
charged on the silver pole in
the more concentrated solu-
tion, forming long crystals of
silver, and silver in equal
amount from the pole in the
dilute solution becomes ionic.

It has been demonstrated
that, for univalent ions, a
*tenfold difference of ionic
concentrations* on the two
sides at ordinary tempera-
tures results in an E.M.F. of
nearly 0.06 volts. A hun-
dred-fold difference gives 0.12 volts, a thousand-fold 0.18 volts,
and so on. For bivalent ions, the corresponding E.M.F. produced

Pos. ions →   Neg. ions ←
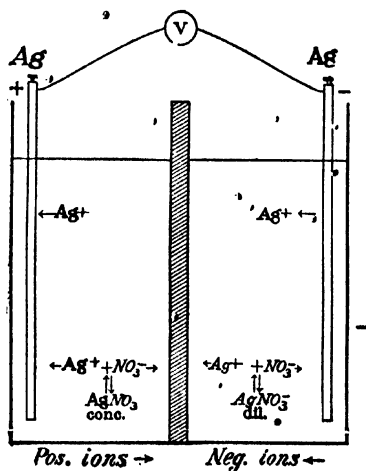
FIG. 134.

are one-half the above values. It is possible, therefore, to use the concentration cell for **measuring solubilities of insoluble salts.** Thus, we cannot easily measure the solubility of silver chloride by the ordinary method (p. 141), because evaporation of the solution may leave a larger mass of impurities, derived from solution of the glass, than of dissolved silver chloride. Hence, we use two poles of silver, place one in normal silver nitrate solution and the other in saturated silver chloride solution (with excess of the solid), measure the difference in potential, and calculate the ratio of the concentrations of silver-ion in the two solutions. The absolute value of that in the silver nitrate solution is known, and so the absolute value of the Ag^+ concentration in the silver chloride solution can be found. Since silver chloride is a salt, it is very highly ionized in so dilute a solution (compare p. 257), and the molecular concentration of silver-ion

is practically equal to the total molecular concentration of silver, and therefore of silver chloride in the liquid.
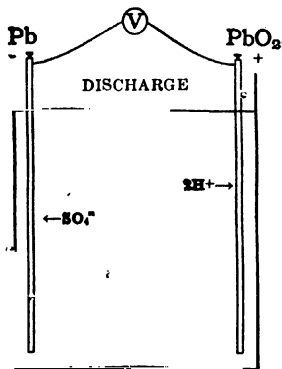
FIG. 135.

The Storage Battery. — In the ordinary **lead accumulator** the plates consist of leaden gratings. The openings in these gratings are filled with finely divided lead in one plate and with lead dioxide in the other. These, and the dilute sulphuric acid in the cell, are the active substances when the cell is charged. When the battery is used as a source of current, the $SO_4^=$ ions migrate towards the plate filled with the lead (Fig. 135), and convert this lead into a mass of the insoluble lead sulphate: $SO_4^= + Pb \rightarrow PbSO_4 + 2\ominus$. This plate, therefore, becomes negatively charged. Simultaneously, the H^+ ions move towards the other plate and there reduce to monoxide the lead dioxide with which it is filled:

$$PbO_2 + 2H^+ + 2\ominus \rightarrow H_2O + PbO.$$
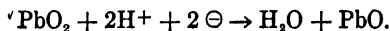
This plate consequently becomes positively charged and, by interaction of the lead monoxide with the sulphuric acid, becomes filled, like the negative plate, with lead sulphate. During the discharge, much sulphuric acid is thus removed from the cell fluid, and the approaching exhaustion of the cells can therefore be ascertained by measuring the specific gravity of the fluid. The E.M.F. of the current is a little over 2 volts (for *normal* ionic concentrations it would be 0.34 + 1.66, or *exactly* 2 volts, see table on p. 656).

The cell may be **recharged** by passing a high-voltage current through the cell, in the opposite direction (Fig. 136). The H^+ ions are attracted to the negative plate and an equivalent number of $SO_4^=$ ions are formed, so that only lead remains:

$$PbSO_4 + 2H^+ + 2 \ominus \rightarrow Pb + 2H^+ + SO_4^=.$$
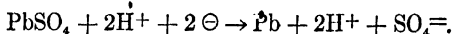
Simultaneously, the $SO_4^=$ is attracted by the positive plate and, with the lead sulphate there present, forms lead disulphate: $SO_4^= + PbSO_4 \rightarrow Pb(SO_4)_2 + 2 \ominus$. The disulphate, being a salt of quadrivalent lead, is at once hydrolyzed (see p. 640), and the filling of this plate is thus changed into lead dioxide: $Pb(SO_4)_2 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4$. Both plates are thus brought back to the condition in which they were before the discharge.

The last set of changes consumes energy, while the first set liberates energy. Both may be stated in a single equation:

$$\text{charge} -$$
$$2PbSO_4 + 2H_2O \rightleftarrows Pb + 2H_2SO_4 + PbO_2.$$
$$\leftarrow \text{discharge}$$
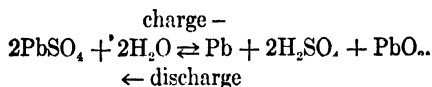
In the **Edison** cell, when charged, one plate is of iron and the other contains nickelic oxide Ni_2O_3. The cell liquid is a solution
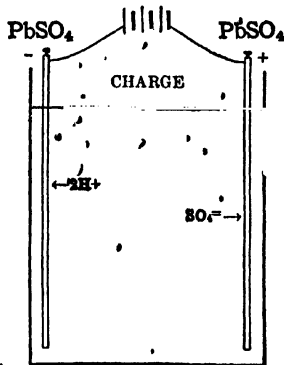
FIG. 136.

of potassium hydroxide. When the cell operates, the nickelic oxide is reduced to $Ni(OH)_2$ and the iron is oxidized to $Fe(OH)_2$, an action, which delivers energy:

$$Fe + 3H_2O + Ni_2O_3 \rightleftharpoons Fe(OH)_2 + 2Ni(OH)_2.$$
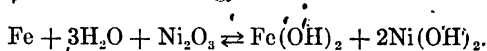
When the cell is recharged, the nickel is reoxidized and the iron reduced.

Exercises. — 1. Make diagrams of the following cells, choosing with care suitable inactive substances to complete the arrangement: (a) chlorine-water and aluminium; (b) chlorine-water and ferrous chloride; (c) zinc and dilute hydrobromic acid; (d) chlorine-water and potassium iodide.

2. Calculate the E.M.F. of each of the cells in Ex. 1, assuming normal solutions to be present.

3. What will be the discharging potentials of solutions of the following substances, assuming N concentrations of the ions: (a) manganous chloride; (b) hydrogen iodide; (c) ferrous bromide; (e) sodium chloride (hydrogen is liberated)?

4. What weight of zinc must be ionized every hour in a cell in order to produce a current of 5 amperes strength? For how long would 500 g. of zinc serve to maintain this current?

5. In the zinc-bromine cell (p. 650), why is the zinc pole called the anode, although its charge with respect to the platinum is negative?

6. What will be the effect upon the E.M.F. of the cell shown in Fig. 131 of adding concentrated ammonium hydroxide in excess to the solution: (a) on the left-hand side, (b) on the right-hand side? Formulate an explanation by means of ionic equations

CHAPTER XLVII

ARSENIC, ANTIMONY, BISMUTH

THIS family is very closely related to the elements phosphorus and nitrogen which precede it in the same column of the periodic table. In reading this chapter, therefore, constant reference should be made to the corresponding compounds of phosphorus.

Each of the three elements **arsenic** (As, at. wt. 74.96), **antimony** (Sb, at. wt. 120.2) and **bismuth** (Bi, at. wt. 209.0) gives two sets of compounds, in which it is trivalent, and quinquivalent, respectively. None of the elements when free displaces hydrogen from dilute acids.

ARSENIC As

The Chemical Relations of the Element. — Arsenic forms a compound with hydrogen AsH_3. It gives several halogen derivatives of the type AsX_3, which are hydrolyzed by water. Its oxides and hydroxides are acidic.

Sulphates, nitrates, carbonates, and other salts of arsenic are not formed. The complex sulphides (p. 667) are important.

Preparation. — **Arsenical pyrites** FeSAs, a mineral similar to pyrite FeS_2, but containing arsenic in place of half of the sulphur, is one of the commonest natural forms of arsenic. When this mineral is heated (air excluded), arsenic passes off as vapor and condenses as a crystalline metallic powder:

$$FeSAs \rightarrow FeS + As \uparrow.$$
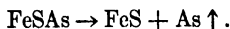
Most other natural sulphides (PbS, FeS_2, SnS_2, $CuFeS_2$, etc.) also contain more or less arsenic. When these ores are oxidized in a draft of air (roasted), the metal, sulphur, and arsenic are all

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converted into oxides. The sulphur dioxide passes off as gas, but the arsenic trioxide As_2O_3 settles in the flues. By distilling the deposit with carbon, free arsenic is obtained:

$$As_2O_3 + 3C \rightarrow 2As \uparrow + 3CO \uparrow.$$
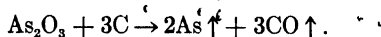
Properties and Uses. — The element has a silvery luster, but tarnishes quickly. When it is heated, its vapor reaches a pressure of 760 mm. before the melting-point is attained, so that the metal sublimes without melting.

The density of the vapor measured at 644° gives 308.4 as the weight of the G.M.V. (22.4 liters at 0° and 760 mm.). The weight of arsenic combining with one chemical unit weight (35.46 g.) of chlorine is 25 g. Three times this amount, or 75 g., is the smallest weight found in the G.M.V. of any volatile compound of arsenic, and is therefore accepted as the atomic weight (p. 97). Since 308.4 is equal approximately to $4 \times 75 (= 300)$, the formula of the vapor of the simple substance at 644° is As_4. At 1700° the formula is As_2 (compare p. 122).

The free element burns in the air, producing clouds of the solid trioxide As_2O_3. It unites directly with the halogens, with sulphur, and with many of the metals. When boiled with nitric acid, chlorine-water, and other powerful oxidizing agents (p. 177), it is oxidized in the same way as is phosphorus, and yields arsenic acid H_3AsO_4.

In the making of **small shot**, about 0.5 per cent of arsenic is added to the lead. The latter is then run into a vessel, with a perforated bottom, placed at the top of the shot tower. The arsenic, like any dissolved substance (p. 155), lowers the freezing-point of the solvent (lead), and delays the solidification of the lead until the drops have assumed perfect spherical form. At the foot of the tower the drops fall into water and are cooled. The arsenic also renders the metal harder than pure lead, and less apt to be deformed during the explosion of the cartridge.

Compounds of arsenic are used in glass works, in making arsenical sprays (mainly calcium arsenate), as weed-killers and insecticides, as cattle and sheep dip, and as hide preservatives.

The normal consumption in the United States amounts to about **16,000** metric tons per year.

Arsine AsH₃. — When arsenic and zinc are melted together in the proportions to form **zinc arsenide** Zn_3As_2, and the product is treated with dilute hydrochloric acid, the result is similar to the action of water or dilute acids upon calcium phosphide, and arsine is evolved as a gas:

$$Zn_3As_2 + 6HCl \rightarrow 2AsH_3 + 3ZnCl_2.$$
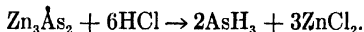
Arsine (arsenuretted hydrogen) is also formed when a solution of arsenious chloride $AsCl_3$ or arsenic acid is added to zinc and hydrochloric acid in a generating flask:

$$AsCl_3 + 3H_2 \rightarrow AsH_3 + 3HCl.$$
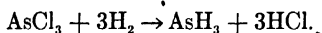
Pure arsine may be secured by leading the mixture with hydrogen through a U-tube immersed in liquid air. The arsine (b.-p. $-55°$) condenses as a colorless liquid (m.-p. $-119°$).

Arsine burns with a bluish flame, producing water and clouds of arsenic trioxide: $2AsH_3 + 3O_2 \rightarrow 3H_2O + As_2O_3$. The combustion of hydrogen containing arsine, generated as just described, gives the same substances. Since arsine, when heated, is readily dissociated into its constituents (compare p. 407), the vapor of free arsenic is present in the interior of the hydrogen flame. This arsenic may be condensed in the form of a metallic-looking, brownish stain by interposition of a cold vessel of white porcelain (Fig. 85, p. 322). This behavior furnishes us with the basis of an exceedingly delicate test — **Marsh's test** — for the presence of arsenic in any soluble form of combination. The compounds of antimony alone show a similar phenomenon (see p. 669).

Arsine is exceedingly **poisonous**, the breathing of small amounts producing fatal effects. Organic derivatives of arsine have been used in warfare as "sneeze-producers" (see p. 599). It differs from ammonia more markedly than does phosphine, for it is not only without action on water or acids, but does not unite directly even with the halides of hydrogen.

Halides of Arsenic. — The trichloride $AsCl_3$, which is prepared by passing chlorine gas into a vessel containing arsenic, is a colorless liquid (b.-p. $130°$). When mixed with water it is at

once converted into the white, almost insoluble trioxide. The action is presumably similar to that of water upon the corresponding compound of phosphorus (p. 274), but the arsenious acid for the most part loses water and forms the insoluble anhydride:

$$AsCl_3 + 3H_2O \rightleftarrows As(OH)_3 + 3HCl,$$
$$2As(OH)_3 \rightleftarrows As_2O_3 \downarrow + 3H_2O.$$
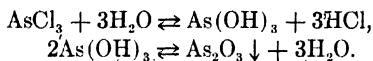
This action, however, differs markedly from the other in that it is *reversible*, since arsenic trioxide interacts with aqueous hydro-chloric acid, giving a solution of arsenious chloride (see p. 469).

Oxides of Arsenic. — Arsenic trioxide As_2O_3 is produced by burning arsenic in the air and during the roasting of arsenical ores (p. 664), and is known as "white arsenic" or simply "arsenic." It is purified for commercial purposes by subliming the flue-dust in cylindrical pots. The pure trioxide is deposited in a glassy form in the upper part of the vessel. Its vapor density shows it to have the formula As_4O_6.

When treated with water, the trioxide goes into solution to slight extent, forming arsenious acid, by reversal of the second of the actions given above. It is an active poison. The fatal dose is 0.06–0.18 g. (1–3 grains), but "arsenic eaters" become tolerant of it and can take four times as much without evil effects.

The **pentoxide** As_2O_5 is a white crystalline substance, formed by heating arsenic acid: $2H_3AsO_4,H_2O \rightarrow As_2O_5 + 4H_2O$. When raised to a higher temperature, it loses a part of its oxygen, leaving the trioxide.

Acids of Arsenic. — When elementary arsenic or arsenious oxide is treated with concentrated nitric acid, or with chlorine and water, **orthoarsenic acid** H_3AsO_4 is produced. The substance crystallizes as a deliquescent white solid $2H_3AsO_4,H_2O$. *Salts* of this acid, and of pyroarsenic acid $H_4As_2O_7$ and metarsenic acid $HAsO_3$, corresponding to the phosphoric acids (p. 410), are known. The chocolate-brown **silver orthoarsenate** Ag_3AsO_4 and the white $MgNH_4AsO_4$, like the corresponding phosphates, are insoluble in water.

Arsenious acid H_3AsO_3, like sulphurous and carbonic acids, loses water, and yields the anhydride (arsenic trioxide) when the attempt is made to obtain it from the aqueous solution. The **potassium** and **sodium arsenites**, K_3AsO_3 and Na_3AsO_3, are made by treating arsenic trioxide with caustic alkalies, and are much hydrolyzed by water. The arsenites of the heavy metals are insoluble, and can be made by precipitation. Scheele's green is an arsenite of copper $CuHAsO_3$. In cases of poisoning by white arsenic, freshly precipitated ferric hydroxide (or the same compound in colloidal suspension) or magnesium hydroxide is administered, since by interaction with the arsenious acid they form insoluble substances.

Sulphides of Arsenic. — **Arsenic pentasulphide** As_2S_5 is obtained as a yellow powder by decomposition of the sulpharsenates (see below), and by leading hydrogen sulphide into the solution of arsenic acid in concentrated hydrochloric acid.

Arsenious sulphide As_2S_3 occurs in nature as orpiment, and was formerly used as a yellow pigment. It is obtained as a citron-yellow precipitate when hydrogen sulphide is led into an aqueous solution of arsenious chloride. When hydrogen sulphide is led into an aqueous solution of arsenious acid, the sulphide is formed, but remains in **colloidal suspension**. It is coagulated by adding solutions of salts (compare p. 554).

Realgar As_2S_2 is a natural sulphide of orange-red color, and is also manufactured by subliming a mixture of arsenical pyrites and pyrite:

$$2FeAsS + 2FeS_2 \rightarrow 4FeS + As_2S_2 \uparrow.$$
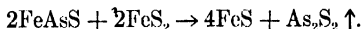
It burns in oxygen, forming arsenious oxide and sulphur dioxide, and is mixed with potassium nitrate and sulphur to make "Bengal lights."

Sulpharsenites and Sulpharsenates. — The sulphides of arsenic interact with solutions of alkali sulphides after the manner of the sulphides of tin (p. 639), giving soluble, complex sulphides. Arsenious sulphide with colorless ammonium sulphide gives ammonium sulpharsenite, and with the yellow sulphide gives ammonium sulpharsenate:

$$3(NH_4)_2S + As_2S_3 \rightarrow 2(NH_4)_3.AsS_3,$$
$$3(NH_4)_2S + As_2S_3 + 2S \rightarrow 2(NH_4)_3.AsS_4.$$
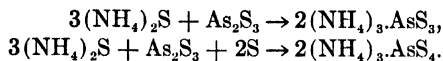
These salts are decomposed by acids, and give the feebly ionized sulpharsenious or sulpharsenic acid:

$$(NH_4)_3.AsS_3 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_3 \rightarrow 3H_2S \uparrow + As_2S_3 \downarrow,$$
$$(NH_4)_3.AsS_4 + 3HCl \rightarrow 3NH_4Cl + H_3AsS_4 \rightarrow 3H_2S \uparrow + As_2S_5 \downarrow.$$
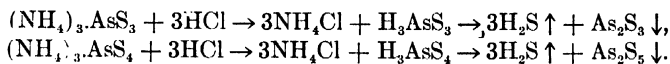
These sulpho-acids, however, at once break up, giving hydrogen sulphide as a gas, and the sulphides of arsenic as yellow precipitates.

ANTIMONY Sb

The Chemical Relations of the Element. — Antimony resembles arsenic in forming a hydride SbH_3 and halides of the forms SbX_3 and SbX_5. The latter are partially hydrolyzed by water. The oxide Sb_2O_3 is basic and also feebly acidic (amphoteric), and the oxide Sb_2O_5 is acidic. The compositions of the compounds are similar to those of the compounds of arsenic, but there are in addition salts, such as $Sb_2(SO_4)_3$, derived from the oxide Sb_2O_3. The element gives complex sulphides.

Occurrence and Preparation. — Antimony occurs free in nature. The sulphide, **stibnite** Sb_2S_3, is also a well-known mineral. When the latter is melted with iron, ferrous sulphide and free antimony are formed:

$$3Fe + Sb_2S_3 \rightarrow 2Sb + 3FeS.$$
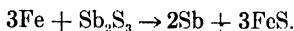
The molten ferrous sulphide (sp. gr. 4.8) floats upon the molten antimony (sp. gr. 6.5), and the products, being mutually insoluble, are easily separated.

The world's production of antimony in 1920 approximated 20,000 metric tons.

Properties. — Antimony is a white, crystalline metal, melting at 630° (b.-p. 1300°). It is brittle, and easily powdered. Its vapor at 1640° has the formula Sb_2, while at lower temperatures Sb_4 is present. It is **used** in making alloys such as type-metal.

stereotype-metal, and britannia metal (see p. 636). The alloys
of antimony expand during solidification, and therefore give ex-
ceptionally sharp castings.

The element unites directly with the halogens. It does not
rust, but when heated it burns in the air, forming the trioxide
Sb_2O_3 or a higher oxide Sb_2O_4. When heated with nitric acid,
it yields the trioxide and, with more difficulty, antimonic acid
H_3SbO_4.

Stibine SbH_3. — The hydride of antimony SbH_3 is formed by
the action of zinc and hydrochloric acid on any soluble compound
of antimony. By the action of dilute, cold hydrochloric acid on
an alloy of antimony and magnesium (1 : 2), a mixture of hy-
drogen and stibine containing as much as 11.5 per cent (by
volume) of the latter may be made. It is separated by cooling
with liquid air (b.-p. $-17°$, m.-p. $-88°$). It is more easily dis-
sociated than is arsine (p. 665), and forms a deposit of an-
timony when a porcelain vessel is held in the flame.

Antimony Halides. —Antimony trichloride $SbCl_3$ is made by
direct union of chlorine and antimony. It forms large, soft
crystals (m.-p. $73°$, b.-p. $223°$), and used to be named "butter
of antimony." When treated with little water, it forms a white,
opaque, insoluble basic salt, antimony oxychloride:

$$SbCl_3 + H_2O \rightleftarrows SbOCl \downarrow + 2HCl.$$
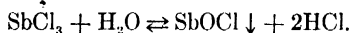
With boiling water the oxide is finally formed. The action is
not complete as long as hydrochloric acid is present, and on
addition of concentrated hydrochloric acid to the mixture, a clear
solution of the trichloride is re-formed.

Oxides of Antimony. — The **trioxide** Sb_2O_3 (vapor density
gives Sb_4O_6) is obtained by oxidizing antimony with nitric acid,
or by combustion of antimony with a limited supply of oxygen.
It is a white substance, insoluble in water. It is in the main
a basic oxide, interacting with many acids to form salts of
antimony. But it interacts also with alkalies, giving soluble
antimonites. The **pentoxide** Sb_2O_5 is a yellow, amorphous sub-
stance, obtained by heating antimonic acid. It combines only

with bases to form salts, and is therefore an acid-forming oxide exclusively. The **tetroxide** Sb_2O_4 is formed by heating antimony or the trioxide in excess of oxygen. It is neither acid- nor base-forming.

Salts of Antimony. —The **nitrate** $Sb(NO_3)_3$ and the **sulphate** $Sb_2(SO_4)_3$ are made by the interaction of the trioxide with nitric and sulphuric acids. They are hydrolyzed by water, giving basic salts. When the trioxide is heated with a solution of potassium bitartrate, KHC_4HO_6, a basic salt $K(SbO)C_4H_4O_6$,-$\frac{1}{2}H_2O$, known as **tartar-emetic**, is formed. This is a white, crystalline substance which is soluble in water and is used in medicine.

Antimonic Acid. — By vigorous oxidation of antimony with nitric acid, or by decomposing the pentachloride with water, a white, insoluble substance of the approximate composition H_3SbO_4 is obtained. This substance interacts with caustic potash and passes into solution. But the salts which have been made are pyro- and metantimoniates. Thus, when antimony is fused with niter, **potassium metantimoniate** $KSbO_3$ is formed. When dissolved, this salt takes up water, giving a solution of the **acid potassium pyroantimoniate:**

$$2KSbO_3 + H_2O \rightarrow K_2H_2Sb_2O_7.$$
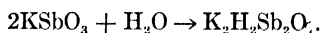
If this is added to a strong solution of a salt of sodium, an **acid sodium pyroantimoniate** is thrown down, $Na_2H_2Sb_2O_7$. This is almost the only somewhat insoluble salt of sodium.

Sulphides of Antimony. —The **trisulphide** Sb_2S_3 is found in nature as the black, crystalline stibnite. As precipitated from solutions of salts of antimony, the trisulphide is an orange-red powder, which, however, after being melted, assumes the appearance of stibnite:

$$2SbCl_3 + 3H_2S \rightleftarrows Sb_2S_3 \downarrow + 6HCl.$$
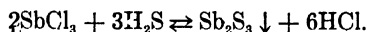
Antimony trisulphide, like cadmium sulphide (p. 565), cannot be precipitated in presence of concentrated hydrochloric acid.

The **pentasulphide** Sb_2S_5 is obtained by the decomposition of the sulphantimoniates (see below). In appearance it resembles the trisulphide and, when heated, decomposes into this substance and free sulphur.

The sulphides of antimony behave towards solutions of the alkali sulphides as do the sulphides of arsenic (p. 667). The trisulphide dissolves in colorless ammonium sulphide with difficulty, forming an unstable, soluble **ammonium sulphantimonite:**

$$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3.$$
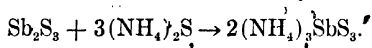
With the pentasulphide or with yellow ammonium sulphide the soluble **ammonium sulphantimoniate** is readily formed:

$$Sb_2S_5 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_4.$$
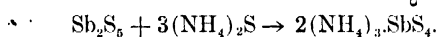
When acids are added to solutions of sulphantimoniates, the sulphantimonic acid which is liberated decomposes, and antimony pentasulphide is thrown down (compare p. 588).

Bismuth Bi

The Chemical Relations of the Element. — Bismuth forms no compound with hydrogen. Its compounds with the halogens are of the form BiX_3 and are hydrolyzed by water giving basic salts. The oxide Bi_2O_3 is basic, and the oxide Bi_2O_5 is not acidic. Bismuth gives a carbonate, nitrate, phosphate, and other salts, in which it acts as a trivalent element. It forms no soluble complex sulphides.

Occurrence and Properties. — This element is found free in nature, and also as trioxide Bi_2O_3 and trisulphide Bi_2S_3. It is a shining, brittle metal with a reddish tinge (m.-p. 270°). Bismuth is one of the few substances (see water) which expand on solidifying. Bismuth is used in preparing *alloys* with very low melting-points. Thus **Wood's metal** contains bismuth (m.-p. 270°) 4 parts, lead (m.-p. 326°) 2 parts, tin (m.-p. 233°) 1 part, and cadmium (m.-p. 320°) 1 part. As is the case with other solutions, the melting-point is lower than that of any of the components, namely 60°. Alloys of this class are used as plugs in sprinkler systems and stops to hold steel fire-doors open.

When, in consequence of a fire, the temperature rises, the alloy melts, the water exits are opened and the fire-doors swing shut. Safety plugs in steam boilers, made of a similar, but less fusible alloy, melt when, as the result of failure of the safety valve, the steam pressure, and therefore 'the temperature, exceeds a predetermined value. They behave in the same way when the water is dangerously low and the metal above the water becomes too hot.

Bismuth does not tarnish, but when heated strongly it burns to form the trioxide. With the halogens it forms a **fluoride** BiF_3, a **bromide** $BiBr_3$, and an **iodide** BiI_3. When the metal is treated with oxygen acids, or the trioxide with any acids, salts are produced.

Compounds of Bismuth. — In addition to the basic **trioxide** Bi_2O_3, which is a yellow powder obtained by direct oxidation of the metal or by ignition of the nitrate, three other oxides are known — BiO, Bi_2O_4, and Bi_2O_5. None of these, however, is either acid-forming or base-forming.

The salts of bismuth, when dissolved in water, give insoluble basic salts, and the actions are reversible, the basic salts being redissolved by addition of an excess of the acid. In the case of the **chloride** $BiCl_3,H_2O$ and the **nitrate** $Bi(NO_3)_3,5H_2O$, the actions taking place are:

$$BiCl_3 + 2H_2O \rightleftarrows Bi(OH)_2Cl + 2HCl,$$
$$Bi(NO_3)_3 + 2H_2O \rightleftarrows Bi(OH)_2NO_3 + 2HNO_3.$$
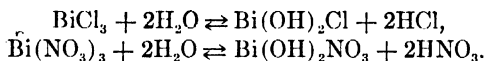
The former of these products, when dried, loses a molecule of water, giving the **oxychloride** $BiOCl$. The **oxynitrate** $Bi(OH)_2NO_3$ is much used in medicine, for the treatment of some forms of indigestion, under the name of "subnitrate of bismuth." It is often contained in face powders.

The brownish-black **trisulphide** Bi_2S_3 may be obtained by direct union of the elements, or by precipitation with hydrogen sulphide. This sulphide is not affected by solutions of ammonium sulphide or of potassium sulphide. It differs, therefore, markedly from the sulphides of arsenic and antimony in its behavior.

Analytical Reactions of Arsenic, Antimony, and Bismuth. — The ions which are most frequently encountered are As^{+++}, Sb^{+++}, Bi^{+++}, $AsO_4^{\equiv}$, and AsO_2^{-}. The first three, with hydrogen sulphide, give colored sulphides which are not affected by dilute acids. The sulphides of arsenic and antimony are separable from the sulphide of bismuth by solution in yellow ammonium sulphide. Marsh's test enables us to recognize the presence of traces of compounds of arsenic and antimony. Oxygen compounds of arsenic, when heated with carbon, give a volatile, metallic-looking deposit of arsenic.

VANADIUM, COLUMBIUM, TANTALUM

These three elements occupy the left-hand side of the sixth column in the periodic system (p. 358). All are rare, but **vanadium** is less uncommon than the others. It is found in rather complex compounds. When these are heated with soda and sodium nitrate, **sodium metavanadate** $NaVO_3$ is formed, and can be extracted with water. The element has very feeble baseforming properties, and gives only a few unstable salts. Ferrovanadium, an alloy, is used in making vanadium steel.

Columbium and **tantalum** also possess feeble base-forming properties, their chief compounds being the columbates and tantalates.

Exercises. — 1. Tabulate the physical and chemical properties of the elements nitrogen, phosphorus, arsenic, antimony and bismuth, and of their compounds with hydrogen and oxygen. Note carefully how the periodic law furnishes valuable aid in systematizing the chemistry of this group (compare p. 354).

2. Formulate the series of changes involved in the solution of arsenic trioxide and the interaction of hydrochloric acid with the arsenious acid so formed (compare p. 327).

3. What is the full significance of the fact that arsenic pentasulphide may be precipitated by hydrogen sulphide from a solution of arsenic acid in hydrochloric acid? Make the equation.

4. Formulate equations for the interactions of arsenious sulphide and antimony trisulphide with yellow ammonium sulphide.

5. Construct equations showing the interaction of, (a) oxygen and arsenical pyrites, (b) chlorine-water and arsenic, (c) the dehydration of orthoarsenic acid, (d) potassium hydroxide and arsenic trioxide, (e) concentrated nitric acid and antimony, (f) potassium bitartrate and antimony trioxide, (g) acids and ammonium orthosulphantimoniate.

6. Would you class arsenic, antimony and bismuth among the metals or among the non-metals? Consider each element separately and give your reasons in each case.

CHAPTER XLVIII

CHROMIUM AND MANGANESE

The chromium (Cr, at. wt. 52.0) family includes molybdenum (Mo, at. wt. 96.0), tungsten (W, at. wt. 184.0), and uranium (U, at. wt. 238.2), and occupies the seventh column of the periodic table along with the sulphur family.

The Chemical Relations of the Family. — The features which are common to the four elements are also those which affiliate them most closely with their neighbors on the right side of the column. They yield oxides of the forms CrO_3, MoO_3, WO_3, and UO_3, which, like SO_3, are acid anhydrides, and show the elements to be sexivalent. They give also acids of the form H_2XO_4, such as chromic acid H_2CrO_4. These acids correspond to sulphuric acid, and their salts, for example the chromates, resemble the sulphates.

Aside from the chromates, the first element forms also two basic hydroxides $Cr(OH)_2$ and $Cr(OH)_3$, from which the numerous chromous (Cr^{++}) and chromic (Cr^{+++}) salts are derived. Uranium is base-forming, as well as acid-forming. Molybdenum and tungsten are not base-forming elements.

CHROMIUM Cr

The Chemical Relations of the Element. — Chromium gives four classes of compounds, and most of them are colored substances (Greek, $\chi\rho\tilde{\omega}\mu\alpha$, color). The chromates are derived from chromic acid H_2CrO_4, which, however, is itself unstable, and leaves the anhydride when the solution is evaporated. The oxide and hydroxide in which the element is trivalent, namely Cr_2O_3 and $Cr(OH)_3$, are weakly basic and still more weakly acidic. Hence we have chromic salts such as $CrCl_3$ and $Cr_2(SO_4)_3$ which are somewhat hydrolyzed, but no carbonate, and no sulphide which is stable in water. The compounds in which the same

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hydroxide acts as an acid arc the chromites, and are derived from the less completely hydrated form of the oxide CrO(OH). Potassium chromite $K.CrO_2$ is more easily hydrolyzed, however, than is potassium zincate or potassium aluminate. Finally, the chromous salts such as $CrCl_2$ and $CrSO_4$ correspond to chromous hydroxide $Cr(OH)_2$ in which the element is bivalent. This hydroxide is more distinctly basic than is chromic hydroxide, and forms a carbonate and sulphide which can be precipitated in aqueous solution.

Occurrence and Isolation. — Chromium is found chiefly in ferrous chromite $Fe(CrO_2)_2$, which constitutes the mineral **chromite.** This is mined chiefly in California, Rhodesia and New Caledonia. The U. S. production in 1918, stimulated by war requirements, exceeded 80,000 tons. In 1921 it sank to less than 300 tons. The metal is easily made by reduction of the oxide with aluminium filings by Goldschmidt's method (p. 583).

Physical and Chemical Properties. — Chromium is a white, crystalline, very hard metal (m.-p. 1520°). It does not tarnish, but when heated it burns in oxygen, giving the green chromic oxide Cr_2O_3. It seems to exist in two states, an active and a passive one, the relations of which are still somewhat obscure. A fragment which has been made by the Goldschmidt method, or has been dipped in nitric acid, is passive, and does not displace hydrogen from hydrochloric acid. When, however, the specimen is warmed with this acid, it begins to interact, and thereafter behaves as if it lay between zinc and cadmium in the electromotive series. If left in the air, it slowly becomes inactive again.

Tin and iron with hydrochloric acid form stannous and ferrous chlorides respectively, because the higher chlorides, if present, would be reduced by the displaced hydrogen. Here, for the same reason, chromous chloride and not chromic chloride is formed:

$$Cr + 2HCl \rightarrow CrCl_2 + H_2, \text{ or } Cr + 2H^+ \rightarrow Cr^{++} + H_2.$$
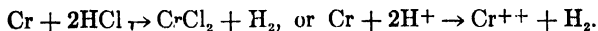
Chromium (3 per cent) is added to harden steel, and with nickel is used in armor-piercing shells and in **armor plate.** Alloys

which, although composed entirely of active metals, are hardly affected even by boiling acids (including nitric acid), usually contain chromium (*e.g.*, 60 per cent Cr, 36 per cent Fe, 4 per cent Mo, no C). Stainless cutlery contains 12 to 14 per cent of chromium.

DERIVATIVES OF CHROMIC ACID

Potassium Chromate K_2CrO_4. — Finely powdered chromite is mixed with potash and limestone, and roasted. The lime is employed chiefly to keep the mass porous and accessible to the oxygen of the air, the potassium compounds being easily fusible:

$$4Fe(CrO_2)_2 + 8K_2CO_3 + 7O_2 \rightarrow 2Fe_2O_3 + 8K_2CrO_4 + 8CO_2.$$
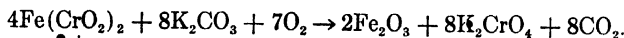
The iron is oxidized to ferric oxide, and the chromium passes from the state of chromic oxide in the chromite (FeO,Cr_2O_3) to that of chromic anhydride in the potassium chromate $(K_2O,-CrO_3)$. The cinder is treated with hot potassium sulphate solution. This interacts with the calcium chromate, which is formed at the same time, giving insoluble calcium sulphate:

$$CaCrO_4 + K_2SO_4 \leftrightarrows CaSO_4 \downarrow + K_2CrO_4.$$
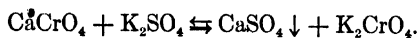
The whole of the potassium chromate goes into solution.

Potassium chromate is pale-yellow in color, gives anhydrous, rhombic crystals like those of potassium sulphate, and is very soluble in water (61 : 100 at 10°).

The Dichromates. — When a solution of potassium sulphate is mixed with an equivalent amount of sulphuric acid, potassium bisulphate is obtainable by evaporation: $K_2SO_4 + H_2SO_4 \rightarrow 2KHSO_4$. The *dry* acid salt, when *heated*, loses water (p..347), giving the pyrosulphate (disulphate): $2KHSO_4 \rightleftarrows K_2S_2O_7 + H_2O$, but the latter, when redissolved, returns to the condition of acid sulphate. The second action is instantly reversed in presence of water. Now, when an acid is added to a chromate we should expect the chromic acid H_2CrO_4, thus liberated, to interact, giving an acid chromate (say, $KHCrO_4$). No acid chromates are known, however, and instead of them, pyrochromates or dichromates are produced, with elimination of water. In other words

the second of the above actions is not appreciably reversible in presence of water when chromates are in question:

$$K_2CrO_4 + H_2SO_4 \rightarrow (H_2CrO_4) + K_2SO_4.$$
$$K_2CrO_4 + (H_2CrO_4) \rightarrow K_2Cr_2O_7 + H_2O.$$
$$\overline{2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + H_2O + K_2SO_4.}$$
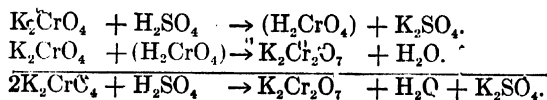
In terms of ions, $S_2O_7^=$ is unstable in water, and interacts with the OH^- ion it contains, giving water and sulphate-ion, while $Cr_2O_7^=$ is stable in water and is formed from the interaction of water and chromate-ion:

$$S_2O_7^= + 2OH^- \leftrightarrows H_2O + 2SO_4^=,$$
$$Cr_2O_7^= + 2OH^- \leftrightarrows H_2O + 2CrO_4^=.$$
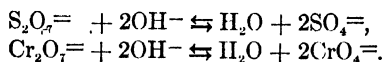
The dichromate of potassium is made by adding sulphuric acid to the crude solution of the chromate obtained from chromite (p. 677). It crystallizes when the liquid cools, and the mother-liquor, containing the potassium sulphate and undeposited dichromate, is used for extracting a fresh portion of cinder. As the dichromates are much less soluble than the chromates, they crystallize from less concentrated solutions, and can therefore be obtained in purer condition. For this reason the extract is always treated for dichromate.

Potassium dichromate $K_2Cr_2O_7$ crystallizes in asymmetric tables of orange-red color (Fig. 48, p. 105). Its solubility in water is 8 : 100 at 10° and 12.5 : 100 at 20°.

Chemical Properties of the Dichromates. — 1. When concentrated sulphuric acid is added to a dichromate, **chromic anhydride** CrO_3 separates in red needles:

$$Na_2Cr_2O_7 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + 2CrO_3 \downarrow.$$
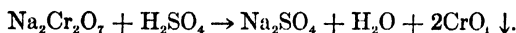
2. Although a dichromate lacks the hydrogen, it is essentially of the nature of an acid salt, just as SbOCl lacks hydroxyl, but is essentially a basic salt. Hence, when potassium hydroxide is added to a solution of potassium dichromate, potassium chromate is formed:

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$
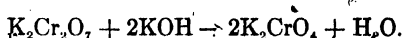
The solution changes from red to yellow, and the chromate is obtained by evaporation. In this way the pure alkali chromates are made.

3. By addition of potassium dichromate to a solution of a salt of a metal whose chromate is insoluble, the chromate and *not* the dichromate is precipitated. This occurs in consequence of the fact that there is always a little hydrogen-ion and $CrO_4=$ in the solution of the dichromate:

$$2Ba(NO_3)_2 + K_2Cr_2O_7 + H_2O \rightleftarrows 2BaCrO_4 \downarrow + 2KNO_3 + 2HNO_3.$$
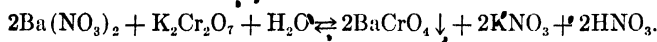
Being essentially an acid salt, the dichromate produces a salt and an acid, as any acid salt would do. For example:

$$Ba(NO_3)_2 + KHSO_4 \rightleftarrows BaSO_4 \downarrow + KNO_3 + HNO_3.$$
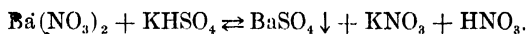
4. The dichromates of potassium and sodium melt when heated and, at a white heat, decompose, giving the chromate, chromic oxide, and free oxygen. To make the equation, we note that the dichromate, for example $K_2Cr_2O_7$, may be written as K_2CrO_4,CrO_3, and the CrO_3, if alone, will decompose thus: $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$. The equation is therefore:

$$4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2.$$
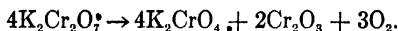
5. With free acids the dichromates give powerful oxidizing mixtures, in consequence of their tendency to form chromic salts. When concentrated hydrochloric acid is used, this acid itself (see pp. 178, 303) suffers oxidation:

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$
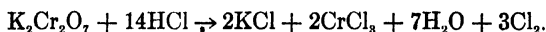
When sulphuric acid is employed, an oxidizable substance such as hydrogen sulphide (compare p. 323), sulphurous acid, or alcohol must be present, if the dichromate is to be reduced. In practice, this sort of action is used for the purpose of making chromic salts, and for its oxidizing effects, as in the preparation of aldehyde and in the dichromate battery.

Uses of Dichromates. — When paper is coated with gelatine containing a soluble chromate or dichromate and, after being dried, is exposed to light, chromic oxide is formed by reduction,

and combines with the gelatine. This product will not swell
up or dissolve in tepid water, as does pure gelatine. This action
is used in many ways for purposes of artistic reproduction. Thus,
if the gelatine mixture is made up with lampblack and, after the
coating has dried, is covered with a negative and exposed to
light, the parts which were protected from illumination may
afterwards be washed away, while the **carbon print** remains. The
gelatine layer can be transferred to wood or copper before wash-
ing. When materials of different colors are substituted for the
lampblack, prints of any desired tint may be made by the same
process.

Sodium dichromate is used, instead of tan-bark, in **tanning**
kid and glove leathers. A reducing agent is employed to pre-
cipitate chromic hydroxide $Cr(OH)_3$ in the leather. Its use
diminishes the time required for the process from 8 or 10 months
to a few hours. The hide is a mixture of colloidal materials,
and the hydroxide is adsorbed.

Insoluble Chromates. — A number of chromates, formed by
precipitation with a solution of a soluble chromate or dichromate,
are familiar. Thus, **lead chromate** $PbCrO_4$ is used as a yellow
pigment. By treatment with limewater it gives a basic salt of
brilliant orange color — **chrome-red** Pb_2OCrO_4. Salts of calcium
give a yellow, hydrated **calcium chromate** $CaCrO_4,2H_2O$ analogous
to gypsum, and, like it, perceptibly soluble in water (0.4 : 100 at
14°). **Barium chromate** $BaCrO_4$ is also yellow. It interacts with
active acids to form the dichromate, and passes into solution. It
is not soluble enough to be attacked by acetic acid. **Strontium
chromate** $SrCrO_4$, however, is soluble in acetic acid. **Silver chro-
mate** Ag_2CrO_4 is red, and interacts easily with acids. It will be
observed that there is a close correspondence between the rela-
tive solubilities (see Table) of the chromates and the sulphates.

CHROMIC AND CHROMOUS COMPOUNDS

Chromic Chloride. — A hydrated chloride $CrCl_3,6H_2O$ is ob-
tained by treating the hydroxide $Cr(OH)_3$ with hydrochloric acid
and evaporating. When heated, this hydrate is hydrolyzed, and
chromic oxide remains. The anhydrous chloride $CrCl_3$ is formed

by·sublimation, as a mass of brilliant, reddish-violet scales, when chlorine is led over heated metallic chromium. In this form the substance dissolves with extreme slowness, even in boiling water, but in presence of a trace, of chromous chloride or stannous chloride it' is easily soluble. The solution is green, as are all solutions of chromic salts after they have been boiled, but on standing in the cold, bluish crystals of $CrCl_3,6H_2O$ are deposited. These give a violet solution with cold water, but boiling reproduces the green color. The difference in the two varieties is due to the different positions in the·hydrated chromic chloride molecule occupied by combined water. From the green solution in the cold, silver nitrate precipitates immediately only one-third of the chlorine as silver chloride.

Chromic ·Hydroxide. — When ammonium hydroxide is added to a solution of a chromic salt, a hydrated hydroxide of pale-blue color, $2Cr(OH)_3,H_2O$, is thrown down. This interacts with acids, giving chromic salts. It also dissolves in potassium and sodium hydroxides to form green solutions of **chromites** of the form $KCrO_2$. When the solutions of the alkali chromites are boiled, the free chromic hydroxide, present in consequence of hydrolysis, is converted into a greenish, less completely hydrated, and less soluble variety. This begins to come out as a precipitate, and soon the whole action is reversed. The hydroxide is used as a mordant (p. 591) and is the active substance in the chrome-tanning process (p. 680).

Chromic Oxide Cr_2O_3. — This oxide is obtained as a green, infusible powder by heating the hydroxide; or, more readily, by heating dry ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4H_2O + Cr_2O_3.$$
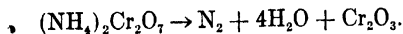
Chromic oxide is not affected by acids, but may be converted into the sulphate by fusion with potassium bisulphate. It is used for making green paint, and for giving a green tint to glass. When the oxide, or any of the chromic salts, is fused with a basic substance such as an alkali carbonate, it passes into the form of a chromate, absorbing the necessary oxygen from the air. If an

alkali nitrate or chlorate is added, the oxidation goes on more quickly.

Chromic Sulphate $Cr_2(SO_4)_3,15H_2O$. — This salt crystallizes in reddish-violet crystals, and may be made by treating the hydroxide with sulphuric acid. When mixed with potassium sulphate, it gives reddish-violet, octahedral crystals of **chrome-alum** (see p. 585), $K_2SO_4,Cr_2(SO_4)_3,24H_2O$. This double salt is most easily obtained by reducing potassium dichromate in dilute sulphuric acid by means of sulphurous acid (p. 679), and allowing the solution to crystallize. The solution of the crystals, either of the pure sulphate or of the alum, is bluish-violet ($Cr+++$), but when boiled becomes green (compare chromic chloride).

Chromous Compounds. — By the interaction of chromium with hydrochloric acid, or by reducing chromic chloride in a stream of hydrogen, **chromous chloride** $CrCl_2$ is formed. The anhydrous salt is colorless, and its solution is light blue ($Cr++$). Like stannous chloride, it is very easily oxidized by the air:

$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O.$$
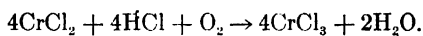
Chromous hydroxide $Cr(OH)_2$ is obtained as a yellow precipitate when alkalies are added to the chloride.

Analytical Reactions of Chromium Compounds. — The chromic salts give the bluish-violet chromic-ion $Cr+++$, or the green complex cations, and may be recognized in solution by their color. The chromates and dichromates give the ions $CrO_4^=$ and $Cr_2O_7^=$, which are yellow and red respectively. From chromic salts, alkalies and ammonium sulphide precipitate the bluish-green hydroxide, and carbonates give a basic carbonate which is almost completely hydrolyzed to hydroxide. By fusion with sodium carbonate and sodium nitrate, they yield a yellow bead containing the chromate. The chromates and dichromates are recognized by the insoluble chromates which they precipitate, and by their oxidizing power when mixed with acids. All compounds of chromium give a green borax bead containing chromic borate, and this bead differs from that given by compounds of copper (see p. 612), both in tint and in being unreducible.

MOLYBDENUM, TUNGSTEN, URANIUM

Molybdenum. — This element is found chiefly in wulfenite $PbMoO_4$ and molybdenite MoS_2. The latter resembles black lead (graphite), and its appearance suggested the name of the element (Greek, μολύβδαινα, lead). The molybdenite is converted by roasting into **molybdic anhydride** MoO_3. · When this is treated with ammonium hydroxide, or with sodium hydroxide, **ammonium molybdate** $(NH_4)_2MoO_4$ or **sodium molybdate** $Na_2MoO_4, 10H_2O$ is obtained. The metal itself is liberated by reducing the oxide or chloride with hydrogen. When pure it is a silvery metal and, like iron (p. 699), takes up carbon and shows the phenomena of tempering. The **oxides** Mo_2O_3, MoO_2, and MoO_3 are known, but the lower oxides are not basic. The **chlorides** Mo_3Cl_6, $MoCl_3$, $MoCl_4$, and $MoCl_5$ have been made. The chief use of molybdenum compounds in the laboratory is in testing for and estimating **phosphoric acid.** When a little of a phosphate is added to a solution of ammonium molybdate in nitric acid, and the mixture is warmed, a copious yellow precipitate of a complex **phosphomolybdate of ammonium** is formed. This compound is soluble in excess of phosphoric acid and in alkalies, but not in dilute mineral acids.

Tungsten. — The minerals scheelite $CaWO_4$ and wolfram $[Fe,Mn]WO_4$ are tungstates of calcium and of iron and manganese, respectively. By fusion of wolfram with sodium carbonate and extraction with water, **sodium tungstate** $Na_2WO_4, 2H_2O$ is secured. It is used as a mordant and for rendering muslin fireproof. Acids precipitate **tungstic acid** H_2WO_4, H_2O from solutions of this salt. The element gives the **oxides** WO_2 and WO_3, the latter being formed by ignition of tungstic acid. The **chlorides** WCl_2, WCl_4, WCl_5, and WCl_6 are known.

The metal (sp. gr. 19.6) can be liberated by reduction of the oxide by hydrogen or by carbon. It has a higher melting point (3540°) than any other metal and, on this account, and because it is less volatile than carbon, is now used for filaments in electric lamps. A carbon filament also requires 3.25 watts per candle power while a tungsten filament uses only 1.25 watts per

1 c. p. The powdered metal obtained by reduction can·be pressed into wire form and then rolled while strongly heated by an electric current until a compact wire is obtained. In 1920, in the United States alone, nearly two hundred million tungsten lamps were manufactured. Shop work has been almost revolutionized by the use of tungsten steel tools (see p. 699).

Uranium. — Pitchblende, which contains the oxide U_3O_8 along with smaller amounts of many other elements, is found mainly in Joachimsthal (Bohemia) and in Cornwall. Carnotite, a uranate and vanadate of potassium $K_2O,2UO_3,V_2O_5,3H_2O$ occurs in Colorado. Pitchblende is roasted with lime, the calcium uranate $CaUO_4$ thus formed is decomposed with sulphuric acid, giving uranyl sulphate UO_2SO_4. When excess of sodium carbonate is added to the solution of the latter, the foreign metals are precipitated and **sodium diuranate** $Na_2U_2O_7,7H_2O$, which is also thrown down, dissolves in the excess as Na_2UO_4.

After filtration, the diuranate of sodium is reprecipitated by neutralizing with sulphuric acid and boiling. This salt is used in making **uranium glass**, which shows a yellowish-green fluorescence. The **oxides** are UO_2 a basic oxide, U_2O_3, U_3O_8 the most stable oxide, UO_3 uranic anhydride, and UO_4 a peroxide. When the oxide UO_2 is treated with acids, it gives uranous salts such as **uranous sulphate** $U(SO_4)_2,4H_2O$. Uranic anhydride and uranic acid interact with acids, giving basic salts, such as $UO_2SO_4,3\frac{1}{2}H_2O$, and $UO_2(NO_3)_2,6H_2O$, which are named **uranyl sulphate, uranyl nitrate,** and so forth. They are yellow in color, with green fluorescence. Ammonium sulphide throws down the brown, unstable **uranyl sulphide** UO_2S from their solutions.

The most striking property exhibited by uranium and its compounds, *radioactivity,* will be dealt with in the final chapter.

MANGANESE

The Chemical Relations of the Element. — Manganese stands, at present, alone on the left side of the eighth column of the periodic table. The right side is occupied by the halogens. It is never univalent, as are the halogens, but its heptoxide

Mn_2O_7 and the corresponding acid, permanganic acid $HMnO_4$, are in many ways closely related to the heptoxide of chlorine and perchloric acid $HClO_4$. Of the lower oxides of manganese, MnO is basic, and Mn_2O_3, feebly basic. MnO_2 is feebly acidic, MnO_3 more strongly so, and permanganic acid (from Mn_2O_7) is a very active acid. Contrary to the habit of feebly acidic and feebly basic oxides, such as those of zinc, aluminium, and tin, the basic oxides of manganese are not at all acidic, and, the acidic oxides, with the exception of MnO_2, are not also basic. There are thus the five following, rather well-defined sets of compounds, showing five different valences of the element. Of these the first, fourth, and fifth are the most stable and the most important.

1. **Manganous compounds,** MnO, $Mn(OH)_2$, $MnSO_4$, etc. These compounds resemble those of the magnesium family (and those of Fe^{++}). The salts of weak acids, such as the carbonate and sulphide, are easily made, and there is little' hydrolysis of, the halides. The salts are pale-pink in color.

2. **Manganic compounds,** Mn_2O_3, $Mn(OH)_3$, $Mn_2(SO_4)_3$, [$MnCl_3$]. The salts resemble the chromic and aluminium salts in behavior, but are even less stable than those of quadrivalent lead. They are completely hydrolyzed by little water. The salts are violet in color.

3. **Manganites,** MnO_2, H_2MnO_3, $CaMnO_3$. ' The alkali manganites are strongly hydrolyzed, like the plumbates and the stannates.

4. **Manganates,** MnO_3, H_2MnO_4, K_2MnO_4. The salts resemble the sulphates and chromates, but are much more easily hydrolyzed. The free acid resembles chloric acid (p. 309) in that, when it decomposes, it yields a higher acid ($HMnO_4$) and a lower oxide (MnO_2). The salts are green in color.

5. **Permanganates,** Mn_2O_7, $HMnO_4$ (hydrated), $KMnO_4$. The salts resemble the perchlorates, and are not hydrolyzed by water. They are reddish-purple in color.

It will be seen that the element manganese changes its character totally with change in valence, and in each form of combination resembles some set of elements of valence identical with that which it has itself assumed. Since the valence represents the number of electrons gained or lost by each atom (p. 267), it

is thus evident that the chemical properties of an element depend more upon the electrical constitution of its atom than upon the atomic weight (see p. 729).

Occurrence and Properties. — The chief ore is the dioxide, **pyrolusite** MnO_2, which always contains compounds of iron. The metal is most easily made by reducing the pulverized dioxide with aluminium by Goldschmidt's method.

The metal manganese (m.-p. 1260°) has a grayish luster faintly tinged with red. It is oxidized superficially by air, and easily displaces hydrogen from dilute acids, giving manganous salts. Its alloys with iron, such as spiegel iron (5–15 per cent Mn) and ferro-manganese (70–80 per cent Mn), are made by using manganese ores with the charge in the blast furnace, and are added to the iron in making special steels. Wire made of an alloy called **manganin** (see p. 476) is used in instruments for making electrical measurements, because its resistance does not alter with moderate changes in temperature.

Oxides. — **Manganous oxide** MnO is a green powder, made by reducing any of the other oxides with hydrogen. **Hausmannite** Mn_3O_4 is dull red. An oxide having this composition is formed when any of the other oxides is heated in air, oxidation or reduction, as the case may be, taking place (compare p. 642). **Manganic oxide,** Mn_2O_3 is brownish-black, and is formed by heating any of the oxides in oxygen.

Manganese dioxide MnO_2 is black, and is most easily prepared in pure condition by gentle ignition of manganous nitrate. Manganese dioxide is not a peroxide (see p. 292); its reaction formula is $O = Mn = O$. It is used for manufacturing chlorine, although electrolytic processes are now driving it out of this field. In glass-making (p. 454), it is employed to oxidize the green ferrous silicate, derived from impurities in the sand, to the pale-yellow ferric compound. The amethyst color of the manganic silicate which is formed, tends also to neutralize this yellow. It is mixed with black paints as a "dryer" (oxidizing agent).

Manganese trioxide MnO_3 is a red, unstable powder. **Manganese heptoxide** Mn_2O_7 is a brownish-green, volatile oil.

'When any of these oxides is heated with an *acid,* a manganous salt is obtained. Salts of this class are, in fact, the only stable substances in which manganese is combined with an acid radical In this action the oxides containing more oxygen than does MnO give off oxygen, or oxidize the acid (see p. 179). When the oxides are heated with *bases,* in the presence of *air,* manganates are always formed. In this case, with oxides containing a smaller proportion of oxygen than MnO_3, oxygen is taken from the air.

Manganous Compounds. — The hydroxide $Mn(OH)_2$ is formed as a white precipitate when a soluble base is added to a solution of a manganous salt. This body passes into solution when ammonium salts are added, and cannot be precipitated in their presence on account of the formation of molecular ammonium hydroxide and the suppression of hydroxide-ion (compare magnesium hydroxide, p. 560). The hydroxide quickly darkens when exposed to the air and passes over into hydrated manganic oxide $MnO(OH)$.

The **sulphide** MnS is obtained as a green, crystalline powder by leading hydrogen sulphide over any of the oxides. A flesh-colored, amorphous **manganous sulphide** MnS (often somewhat hydrated) is more familiar and is precipitated by ammonium sulphide from manganous salts. It interacts with active acids and even with acetic acid, so that it cannot be precipitated by the action of hydrogen sulphide on salts (compare p. 329). When rubbed in a mortar it becomes crystalline, and is then green.

The manganous salts of weak acids, such as the carbonate and sulphide, darken when exposed to air and are oxidized, with formation of hydrated manganic oxide. While there is a general resemblance between the manganous salts and the stannous, chromous, and ferrous salts, the manganous salts of active acids are not oxidized by the air as are the corresponding salts of the other three metals.

Manganic Compounds. — The base of this set of compounds, **manganic hydroxide** $Mn(OH)_3$, is slowly deposited by the action of the air on an ammoniacal solution of a manganous salt in

salts of ammonium. **Manganic chloride** $MnCl_3$ is present in the liquid obtained by the action of hydrochloric acid upon man-- ganese dioxide (see p. 178), but loses chlorine very readily.

Manganites. — Although manganese dioxide interacts when fused with potassium hydroxide, simple salts derived from H_2MnO_3 ($= H_2O,MnO_2$) or H_4MnO_4 ($= 2H_2O,MnO_2$) are not formed. The products are complex, as $K_2Mn_5O_{11}$. Some less complex manganites are formed by mixing manganous chloride solution with slaked lime, and blowing air through the mass of, calcium and manganous hydroxides which is thus obtained. Manganites of calcium, such as $CaMnO_3$ ($= CaO,MnO_2$) and $CaMn_2O_5$ ($= CaO,2MnO_2$) are thus formed:

$$Ca(OH)_2 + 2Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3H_2O.$$
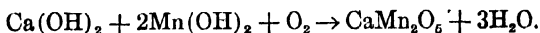
Manganates. — When one of the oxides of manganese is fused with potassium carbonate and potassium nitrate, a green mass is obtained. The green aqueous extract deposits **potassium manganate** K_2MnO_4 in rhombic crystals, which are of the same form as those of potassium sulphate, and are almost black:

$$K_2CO_3 + MnO_2 + O \rightarrow K_2MnO_4 + CO_2.$$
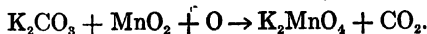
The acid H_2MnO_4 is itself unknown. The potassium salt remains. unchanged in solution only in presence of free alkali. When the concentration of the hydroxide-ion is reduced by dilution, or, better still, when a weak acid such as carbonic acid or acetic acid is used to neutralize it, the salt is decomposed according to the following equation:

$$3K_2MnO_4 + 2H_2O \rightarrow 4KOH + 2KMnO_4 + MnO_2.$$

That is, a precipitate of manganese dioxide and a solution of potassium permanganate are obtained. In terms of the ions (see p. 303) the equation is simpler:

$$3MnO_4^= + 2H^+ \rightarrow 2OH^- + 2MnO_4^- + MnO_2.$$
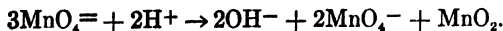
Permanganates. — Potassium permanganate $KMnO_4$ is made by decomposition of the manganate as shown above, and is ob-

tained, in purple crystals with a greenish luster, by evaporation of the solution. To avoid the loss of manganese thrown down as dioxide, the action is carried out commercially by passing ozone through the solution of the manganate: $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + O_2 + 2KOH$. Sodium permanganate $NaMnO_4$ is made in a similar manner; its aqueous solution is known as "Condy's disinfecting fluid." Permanganic acid is a very active acid, that is, it is highly ionized in aqueous solution. When a very little dry, powdered potassium permanganate is moistened with concentrated sulphuric acid, brownish-green, oily drops of permanganic anhydride (manganese heptoxide) Mn_2O_7 are formed. This compound is volatile, giving a violet vapor, and is apt to decompose explosively into oxygen and manganese dioxide. Its oxidizing power is such that combustibles like paper, ether, and illuminating gas are set on fire by contact with it.

Potassium Permanganate as an Oxidizing Agent. — The actions are different according as the substance is employed (1) in alkaline, or (2) in acid solution.

1. When an alkali, such as potassium hydroxide, is added, the action by which the permanganate is formed is reversed, and the solution becomes green from the production of the manganate:

$$4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2,$$

or $\quad 4MnO_4^- + 4OH^- \rightarrow 4MnO_4^= + 2H_2O + O_2.$
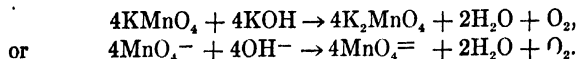
When a substance capable of being oxidized is present, the reduction proceeds further and manganese dioxide is precipitated.

2. In presence of an acid, and an oxidizable body, a manganous salt is always formed. An example of this type (the oxidation of hydrochloric acid to chlorine) has already been discussed in detail (pp. 177, 304).

The quantity of a ferrous salt in a sample of a solution may be measured by titrating (p. 262) the solution with a standard solution of potassium permanganate until the color ceases to be destroyed, and then noting the volume used. For convenience, the standard solution may be prepared so that 1 cc. will oxidize 0.01 g. of Fe^{++}.

3. When **dry** potassium permanganate is heated, it decomposes as follows:

$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2.$$

The fingers are stained brown by an aqueous solution, receiving a deposit of manganese dioxide, in consequence of the reducing power of the unstable organic substances in the skin. The destruction of minute organisms by Condy's fluid results from a similar 'action.' When the powdered salt is moistened with glycerine, the mass presently bursts into flame.

Analytical Reactions of Manganese Compounds. — The ions commonly encountered are manganous-ion Mn^{++}, which is very pale-pink in color, permanganate-ion MnO_4^-, which is purple, and manganate-ion $MnO_4^=$, which is green. The manganous compounds give with ammonium sulphide the flesh-colored sulphide, which is soluble in acids. Bases give the white hydroxide, which darkens by oxidation, and is soluble in salts of ammonium. All compounds of manganese confer upon the borax bead an amethyst color (manganic borate), which, in the reducing flame, disappears (manganous borate). A bead of sodium carbonate and niter becomes green on account of the formation of the manganate.

Exercises. — 1. What do we mean by saying that, (a) chromous chloride is stable (p. 43), but easily oxidized by the air, (b) permanganic acid is an active oxidizing agent in presence of an acid (p. 689).

2. Formulate the oxidations of hydrogen sulphide, of ferrous sulphate, of oxalic acid $H_2C_2O_4$ (to carbon dioxide), and of nitrous acid (to nitric acid) by potassium permanganate in acid solution. In doing so, employ the two methods suggested on pp. 301-305.

3. Construct equations, showing the interactions of: (a) chromic oxide and aluminium, (b) strontium nitrate and potassium dichromate in solution, (c) potassium hydroxide and chromic hydroxide, and the reversal on boiling, (d) chlorine and

potassium chromite in excess of alkali (what is the actual oxi-dizing agent?).

4. What volume of oxygen at 0° and 760 mm., (a) is obtainable from one formula-weight of potassium dichromate, (b) is required to oxidize one formula-weight of chromous chloride?

5. Make equations for all the reactions involved in the preparation of sodium diuranate from pitchblende.

CHAPTER XLIX

IRON, COBALT AND NICKEL

THE elements iron (Fe, at. wt. 55.84), cobalt (Co, at. wt. 58.97), and nickel (Ni, at. wt. 58.68) are neighboring members of the first long period, lying between its first and second oc-taves (see table of periodic system, p. 358).

IRON Fe

Chemical Relations of the Element. — The oxides and hydroxides FeO and $Fe(OH)_2$, Fe_2O_3 and $Fe(OH)_3$ are basic, the former more strongly so than the latter. The ferrous salts, derived from $Fe(OH)_2$, resemble those of the magnesium group and those of Cr^{++} and Mn^{++}, and are little hydrolyzed. The ferric salts, derived from $Fe(OH)_3$, resemble those of Cr^{+++} and Al^{+++} and are hydrolyzed to a considerable extent. Iron gives also a few ferrates K_2FeO_4, $CaFeO_4$, etc., derived from an acid H_2FeO_4 which, like manganic acid H_2MnO_4 (p. 688), is too unstable to be isolated. Complex anions containing iron, such as the anion of $K_4.Fe(CN)_6$, are familiar, but complex cations containing ammonia (see p. 564) are unknown.

Occurrence. — Free iron is found in minute particles in some basalts, and many meteorites are composed of it. Meteoric iron can be distinguished from specimens of terrestrial origin by the fact that it contains 3-8 per cent of nickel. The chief ores of iron are the oxides, hæmatite Fe_2O_3 and magnetite Fe_3O_4, and the carbonate $FeCO_3$, siderite. The first is reddish and radiated in structure; but black, shining, rhombohedral crystals, known as specularite, are also found. Hydrated forms, like brown iron ore $2Fe_2O_3,3H_2O$, are also common. Siderite is pale-brown in color and rhombohedral, like calcite. When mixed with clay it forms iron-stone, from which most of the iron in Great Britain, but less

than one per cent of that in the United States, is obtained. Pyrite FeS_2 consists of golden-yellow, shining cubes or pentagonal do-decahedra. It is used, on account of its sulphur, in the manufacture of sulphuric acid, but, from the oxidized residue, iron of sufficient purity is obtained with difficulty. Compounds of iron are contained in chlorophyll and in the blood (hæmoglobin), and doubtless play an important part in connection with the vital functions of these substances.

Metallurgy. The Blast Furnace. — The ores of iron are first roasted in order to decompose carbonates and oxidize sulphides, if these salts are present. Coke is then used to reduce the oxides. The carbon monoxide CO, produced by the burning of the coke and air, is the actual reducing agent:

$$Fe_3O_4 + CO \rightleftarrows 3FeO + CO_2.$$
$$FeO + CO \rightleftarrows Fe + CO_2.$$
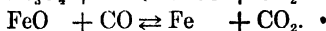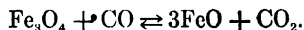
Since the ores contain rocky material (gangue), such as silica SiO_2 and silicates of aluminium, *limestone* is added in the proportion required to give a fusible slag.

The blast furnace (Fig. 137) is an iron structure 40 to 100 feet high, lined with fire-brick. A circular pipe delivers a blast of pre-heated compressed air to several nozzles T (tuyères) near the foot. The ore, coke and limestone are admitted at the top. Reduction of the ore occurs continuously as the solid materials, passing downwards, become hotter and hotter through combustion of the coke. The melted iron and slag (immiscible) finally collect in two layers in the hearth or crucible at the bottom.

Fig. 137.

From time to time the slag is allowed to flow from an opening near the top of the crucible, and the iron from a similar opening
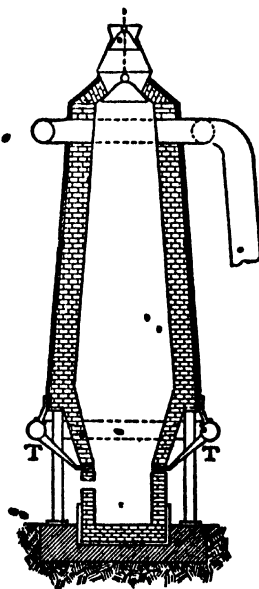
at the bottom. Plugs of wet clay close the openings and are instantly baked hard. The iron is taken in ladles to other parts of the plant, or is cast into "pigs" in steel moulds and chilled in water.

Reactions in the 'Blast Furnace. — The actions (see equations above) are both *reversible* and the carbon dioxide formed tends to react to reproduce the original materials. At any particular temperature it is necessary therefore to keep the proportion of CO_2 to CO in the furnace gases below a certain value in order to prevent the reversal of the reactions. This proportion of CO_2 to CO is regulated, however, by a third reversible reaction:

$$C + CO_2 \rightleftarrows 2CO.$$
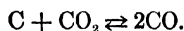
At high temperatures (above 1000°) this reaction is almost complete in the forward direction. As the temperature falls, the proportion of CO_2 in the equilibrium mixture increases rapidly.

If all three reactions had time to attain equilibrium conditions in the blast furnace, reduction of Fe_3O_4 to FeO, and of FeO to Fe, would occur at about 645° and 700° respectively, and the residual gases would contain very little CO. In practice, however, the slowness of the reactions necessitates the use of much higher temperatures and a large excess of CO. The gases that escape are therefore *combustible,* and are led off through openings near the top of the furnace and used for pre-heating the air-blast.

In 1920, nearly 40,000,000 tons of **pig iron** were produced in the United States. The production in Great Britain exceeded 8,000,000 tons. These figures are much lower than the normal, owing to trade depression. The maximum world's output, 79,-000,000 tons, was in 1913.

Cast Iron. — Pure iron is not manufactured, and indeed would be too soft for most purposes. Piano-wire, however, is about 99.7 per cent pure. The product obtained from the blast furnace (**pig iron**) contains 92–94 per cent of iron along with 2.6–4.3 per cent of carbon, often nearly as much silicon, varying

proportions of manganese, and some phosphorus and sulphur.
The last four ingredients are liberated from combination with
oxygen by the carbon in the hottest part of the furnace and
combine or alloy themselves with the iron. Cast iron does not
soften before melting, but melts sharply at 1150–1250° according
to the amount of foreign material it contains. When *suddenly*
cooled it gives chilled cast iron, all the carbon of which is present
in the form of carbide of iron Fe_3C (cementite) in solid solution
in the metal. This solid solution is exceedingly *hard*, but very
brittle. By slower cooling, opportunity is permitted for the sepa-
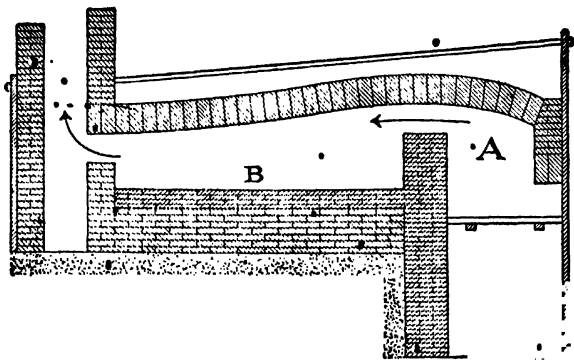
Fig. 138.

ration of part of the carbon as graphite, which appears in tiny
black scales, and gray cast iron results. This mixture is much
softer, on account of the amount of free, relatively pure iron
which it contains.

Cast iron is used in making cooking ranges, stoves, pipes,
and radiators. It expands in solidifying, and so fills every detail
of the mold.

Wrought iron. — Wrought iron, invented by Henry Cort
(1784), is made by heating the broken pigs of cast iron upon a
layer of material containing oxide of iron and hammer-slag
(basic silicate of iron) spread on the bed of a reverberatory fur-
nace (Fig. 138). The flames and heated gases coming over from
the furnace A, deflected by the low roof, play directly upon the

iron in the bed *B* and melt it. The carbon, silicon, and phosphorus combine with the oxygen of the oxide, and 'the last two' pass into the slag. The sulphur is found in the slag as ferrous sulphide. ' On account of the effervescence due to the escape of carbon monoxide, the process is called, "pig-boiling." The iron is stirred with 'iron rods ("puddled") and stiffens as it becomes purer, until finally it can be withdrawn in balls ("blooms") and partially freed from slag by rolling. The resulting bars are • repeatedly cut, piled in 'a bundle, reheated, and rolled. The iron now softens sufficiently for welding below 1000° and melts at, 1500°. ' Its *fibrous structure* is due partly to the films of slag which have not been completely pressed out by the rolling. On account of its *toughness,* wrought iron is used for anchors, chains, and bolts, and for drawing into wire. On account of its relative purity (99.8–99.9 per cent), it is less fusible than cast iron and is used for fire bars. The above operations are now largely displaced by the Bessemer and open hearth processes in which iron of equal purity can be obtained.

Properties of Steel. — This is a variety of iron almost free from phosphorus, sulphur, and silicon. Tool-steel contains 0.9–1.5 per cent of carbon, structural steel only 0.2–0.6 per cent, and mild steel 0.2 per cent or even less. Steel combines the properties of cast and of wrought iron, being *hard* and *elastic,* and at the same time available for forging and welding when the proportion of carbon is not too high. Steel can be *tempered* (see p. 699). It has also a greater *tensile strength* (see p. 467) than

has wrought iron, and it can be *permanently magnetized.*
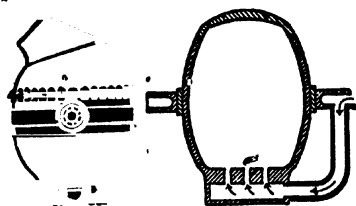
The world's production of steel in 1921 approximated 40,000,000 tons. In 1917 the output exceeded 85,000,000 tons.

<center>FIG. 139.</center>

Bessemer Process. — Steel is made largely by the Bessemer process (Kelly 1852, Bessemer 1855). The molten cast iron is poured into a converter (Fig. 139) and a blast of air is blown through it from tuyères at the

bottom. .The oxidatioñ of the manganese, carbon, silicon, and a little of thê iron gives out sufficient heat to raise the temperature of the mass above the melting-point of wrought iron. The required proportion of carÊop is then introduced by adding pure cast iron, spiegel iron, oŋ coke, and the contents, first the slag and then the molten steel, are finally poured out by turning the converter. When the cast irbn contains much phosphorus, tñe oxide of this elemeñt is reduced again by tÿe iron as fast as it is
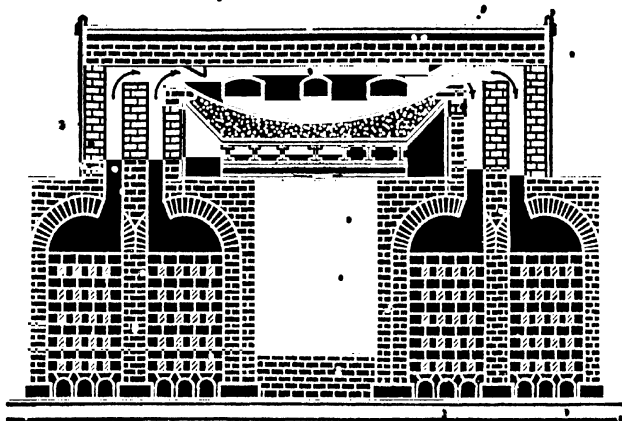
Fig. 140.

formed by the blast. In such cases a basic lining, containing lime and magnesia takes the place of the sand and clay lining of the ordinary Bessemer converter, and a slag containing a basic phosphate of calcium is produced. This modification constitutes what is known as the basic or Thomas-Gilchrist process.• The slag ("Thomas-slag") wheñ pulverized forms a valuable fertilizer (see p. 527). Bessemer steel is used for heavy and light machinery castings, and is rolled into bridge and structural iron. It contains from 0.1 per cent (soft) to 1 per cent (hard) of carbon. In the United States, the basic open-hearth process is preferred.

Open-Hearth (Siemens-Martin) Process. — In this process the cast iron is melted in a saucer-shaped depression (Fig, 140),

which is lined with sand in the acid process and with lime and magnesia in the basic process. Scraps of iron plate (for dilution) and hæmatite, or some other oxide ore, are then added in proper proportions. The materials (50–75 tons in one charge) are heated with gas fuel for 8–10 hours, To secure economically the high temperature required to keep the product (almost pure iron) fused, Siemens devised the method of preheating the fuel gas and air by a regenerative device. The spent air and gas pass down through a checkerwork of brick. When this becomes heated, the valves are reversed, the gas and air now enter through the heated brickwork and, after meeting and burning over the iron, pass out through the checkerwork on the opposite side, raising its temperature in turn.

The changes are similar to those in the Bessemer process. During casting, some aluminium is added to combine with oxygen (present as CO) and give sounder ingots. Recently, iron containing 10–15 per cent of **titanium** has been added instead. The titanium combines with both nitrogen and oxygen and the compounds pass into the slag, just as does aluminium oxide. Rails made of steel purified with this element are less liable to breakage (the commonest cause of wrecks) and are 40 per cent more durable than are ordinary open-hearth rails.

The advantage of the open-hearth process over that of Bessemer is that it is not hurried, and is therefore under better control. The material can be tested by sample at intervals until the required composition has been reached. The product is of more uniform quality. When fine steel is required, electric heating (*e.g.,* in the Héroult furnace) permits even more deliberate treatment.

Open-hearth steel is used for the better class of rails, for railway bridges, for shafts, armor-plate, and heavy guns, and wherever the steel is subject to much vibration.

Crucible Steel. — For special purposes steel is made in crucibles of clay (or graphite and clay) in melts of 60–100 pounds. "Melting bar," a very pure open-hearth steel, is melted with charcoal or with pure pig iron. Crucible steel is employed in making razors (1.5 per cent C), tools (1 per cent C), dies (0.75 per cent C), pens, needles, and cutlery.

Tempering. — To understand this property, it must be noted that carbon dissolves readily in molten iron, and is partly converted to, a *carbide of iron* (Fe_3C, 6.6 per cent C by weight) in solution. As the temperature falls, the solubility of carbon in iron diminishes. When white-hot steel (up to 2 per cent C) is *suddenly chilled,* there is no time for any changes to occur during the cooling, and a supersaturated *solid solution* is obtained which is very hard and brittle. When, however, the cooling is slow, some of the carbon separates in minute crystals of cementite, carbide of iron Fe_3C, until at about 700° where remains only 0.9 per cent of carbon in solution. At this temperature the solid solution breaks down into a mechanical mixture of pure iron which is soft, and carbide of iron which is hard. Steel is thus a mixture, and not homogeneous, when slowly cooled. When therefore hard, chilled steel is heated once more for the purpose of tempering, the extent to which the softer material is formed, depends on the temperature reached, and on the rate and duration of the cooling permitted. By varying these the degree of hardness allowed to remain can be adjusted.

Steel Alloys. — We must distinguish between manganese, aluminium, silicon, or titanium added in small amounts ("medicine") to purify the iron, and passing (in combination) into the slag, as described in preceding sections, and the present subject, which concerns *metals added* so as to produce *regular alloys.*

Manganese steel (7 to 20 per cent Mn) is exceedingly hard even when cooled slowly. It therefore does not lose its temper readily when heated by friction. It is used for the jaws of rock-crushing machinery and for burglar-proof safes.

Chromium-vanadium steel (1 per cent Cr, 0.15 per cent V) has great tensile strength, can be bent double while cold, and offers great resistance to changes of stress, and to torsion. It is used for frames and axles of automobiles, and for connecting rods.

Tungsten steel (tungsten 8 to 20 per cent, and chromium 3 to 5 per cent) is used for tools in high-speed metal turning, as it can become red hot (from friction) without loss of temper.

Nickel steel (containing 2 to 4 per cent of nickel) resists corrosion, and has a very high limit of elasticity and great hardness. It is used for armor-plate, wire cables, and propeller shafts. The alloy with 36 per cent nickel, called invar, is practically non-expansive when heated and is valuable for meter-scales and pendulum rods.

Duriron or tantiron (15 per cent Si) is rustproof and is not attacked by sulphuric, nitric or acetic acid, hot or cold, dilute or concentrated. Vessels made of this alloy are therefore used industrially in acid concentrations.

Chemical Properties of Iron. — Although the purest iron does not rust in cold water, ordinary iron rusts in moist air (p. 9), or under water. Corrosion takes place extremely slowly in water free from carbon dioxide, but the action is greatly hastened by the presence of carbonic acid. Rust is a brittle, porous, loosely adherent coating of variable composition, consisting mainly of a hydrated ferric oxide $3Fe_2O_3.H_2O$, which does not protect the metal below. Oil protects iron from rusting because, although oxygen is more soluble in most oils than in water, and so reaches the iron freely, water is not soluble in oil and so moisture is excluded.

Iron burns in oxygen, and acts when heated upon steam, in both cases producing magnetic oxide of iron Fe_3O_4 (p. 36). A thin film of this oxide is adherent, and protects the iron ("Russia" iron). The articles to be treated are put into a closed retort and exposed first to a current of superheated steam and then to a current of producer gas (p. 426) to reduce any higher oxides that may have been formed. Watch hands, buckles and the like may be given a protective coating by dipping them in an oxidizing bath such as melted saltpeter. Another method of rust proofing is to immerse iron articles in a hot solution of *ferrous phosphate*. This salt is appreciably hydrolyzed in solution, and the free acid acting upon the iron converts its surfaces into an adherent film of basic phosphate.

Iron displaces hydrogen easily from dilute acids. Steel and cast iron, which contain iron, its carbide, and graphite, give with cold dilute acids almost pure hydrogen, and the carbide

and graphite remain unattacked. More concentrated acids, however, particularly when warm, generate, along with hydrogen, hydrocarbons formed by interaction with the carbide (p. 474). The odor of the resulting gas is due to compounds of sulphur and phosphorus.

Although iron acts vigorously on dilute or concentrated nitric acid, it is indifferent to fuming nitric acid. (NO_2 in solution, p. 390). It becomes **passive**. In this state, it no longer displaces hydrogen from dilute acids. If dipped in cupric sulphate solution, it does not receive the usual red coating of metallic copper. However, if the metal is scratched or struck, the passive condition is destroyed, and copper begins to be deposited at the point touched and the action spreads quickly over the whole surface. No satisfactory explanation of this phenomenon has been obtained, although it is shown also by chromium, cobalt, and other metals.

Ferrous Compounds. — **Ferrous chloride** is obtained as a pale-blue hydrate $FeCl_2,4H_2O$ (turning green in the air) by interaction of hydrochloric acid with the metal or the carbonate. The anhydrous salt sublimes in colorless crystals when hydrogen chloride is led over the heated metal. In solution the salt is oxidized by the air to a basic ferric chloride:

$$4Fe^{++} + O_2 + 2H_2O \rightarrow 4Fe^{+++} + 4OH^-.$$
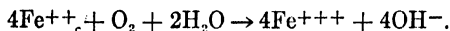
In presence of excess of the acid, normal ferric choride is formed. With nitric acid, ferric chloride and nitric oxide are produced (p. 397).

Ferrous hydroxide $Fe(OH)_2$ is thrown down as a white precipitate, but rapidly becomes dirty-green and finally brown, by oxidation. It dissolves in solutions of salts of ammonium, being like magnesium (hydroxide (p. 560), sufficiently soluble in water to require an appreciable concentration of OH^- for its precipitation. **Ferrous oxide** FeO is black, and is formed by cautious reduction of ferric oxide by hydrogen (at about 300°). It catches fire spontaneously when exposed to the air.

Ferrous carbonate $FeCO_3$ is found in nature as siderite, and may be made in slightly hydrolyzed form by precipitation. The

precipitate is white but rapidly darkens and finally becomes brown, the ferrous hydroxide produced by hydrolysis being oxidized to the ferric condition. The salt interacts with water containing carbonic acid, after the manner of calcium carbonate (p. 425), giving $FeH_2(CO_3)_2$, and hence is found in solution in natural (chalybeate) waters.

Ferrous sulphide FeS may be formed as a black, metallic-looking mass by heating together the free elements. It is produced by precipitation with ammonium sulphide, but not with hydrogen sulphide. It interacts readily with dilute acids. The precipitated form is slowly oxidized to ferrous sulphate by the air.

Ferrous sulphate is obtained by allowing pyrites to oxidize in the air and leaching the residue:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4.$$
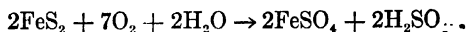
The liquor is treated with scrap iron and the neutral solution evaporated until a hydrate $FeSO_4,7H_2O$, green vitriol, or "copperas," is deposited. The crystals are efflorescent, and become also brown from oxidation to a basic ferric sulphate:

$$4FeSO_4 + O_2 + 2H_2O \rightarrow 4Fe(OH)SO_4.$$
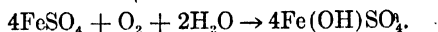
With excess of sulphuric acid and air, or an oxidizing agent such as nitric acid, ferric sulphate is formed. The ferrous sulphate is used in dyeing, in making writing-ink (see p. 706) and rouge (p. 703), and in the purification of water (p. 586).

Ferric Compounds. — By leading chlorine into a solution of ferrous chloride, and evaporating until the proper proportion of water alone remains, a yellow, deliquescent **hexahydrate** of **ferric chloride**, $FeCl_3,6H_2O$ is obtained. When this is heated still further, hydrolysis takes place and the oxide remains. When chlorine is passed over heated iron, **anhydrous ferric chloride** sublimes in dark green scales, which are red by transmitted light. In solution, the salt, like other ferric salts, can be reduced to the ferrous condition by boiling with iron. The same reduction is effected by hydrogen sulphide:

$$2Fe^{+++} + Fe \rightarrow 3Fe^{++}.$$
$$2Fe^{+++} + S^= \rightarrow 2Fe^{++} + S\downarrow.$$
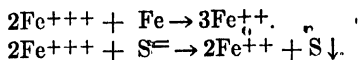
The ferric ion is almost colorless, the yellow-brown color of solutions of ferric chloride being due to the presence of ferric hydroxide produced by hydrolysis. The color deepens when the solution is heated (increased hydrolysis), and fades again very slowly, by reversal of the action, when the cold solution is allowed to stand.,

Ferric hydroxide $Fe(OH)_3$ appears as a brown precipitate when a base is added to a ferric salt. It does not interact with excess of the alkali. In this form the substance dries to the oxide without giving definite intermediate hydrated oxides. The hydrates, $Fe_2O_3,2Fe(OH)_3$ (brown iron ore) and $Fe_2O_3,4Fe(OH)_3$ (bog iron ore), however, are found in nature. The hydroxide passes easily into colloidal solution in a solution of ferric chloride, and by subsequent dialysis through a piece of parchment the salt can be separated, and a pure colloidal suspension of the hydroxide obtained.

Ferric oxide, Fe_2O_3, is sold as "rouge" and "Venetian red." It is made from the ferrous sulphate obtained in cleaning iron ware which is to be tinned or galvanized (see p. 636). The salt is allowed to oxidize, and the ferric hydroxide, thrown down by the addition of lime, is calcined. The product varies in tint from a bright yellowish-red to a dark violet-brown according to the fineness of the powder. The best rouge is obtained by calcining ferrous oxalate FeC_2O_4. This oxide is not distinctly acidic, but by fusion with more basic oxides, compounds like franklinite $Zn(FeO_2)_2$ may be formed. It is reduced by hydrogen, at about 300° to ferrous oxide, and at 700–800° to metallic iron.

Magnetic oxide of iron Fe_3O_4 or lodestone is found in nature, and is formed by the action of air (hammer-scale), steam, or carbon dioxide on iron. It forms octahedral crystals, and is a ferrous-ferric oxide FeO,Fe_2O_3 or $Fe(FeO_2)_2$, related to franklinite.

Ferric sulphide Fe_2S_3 may be made by fusing together the free elements, and is obtained also, as a precipitate by the addition of ammonium sulphide to ferric chloride solution. With hydrogen sulphide, only sulphur is thrown down (p. 702).

Ferric sulphate $Fe_2(SO_4)_3$ is formed by oxidation of ferrous

sulphate, and is obtained as a white mass by evaporation. It gives alums (p. 585), such as ferric-ammonium alum ⸱(NH₄)₂SO₄,- Fe₂(SO₄)₃,24H₂O, which are almost colorless when pure, but usually have a pale reddish-violet tinge.

Pyrite. — The mineral pyrite FeS₂ (Fools' gold) is the sulphide of iron which is most stable in the air. It is not attacked by dilute acids, but concentrated hydrochloric acid slowly converts it into ferrous chloride and sulphur." It is reduced by hydrogen to ferrous sulphide.

Cyanides. — When potassium cyanide is added to solutions of ferrous or ferric salts, yellowish precipitates are produced, but the simple cyanides cannot be obtained in pure form. These precipitates interact with excess of the cyanide giving soluble complex cyanides. These are called ferro- and ferricyanide of potassium, respectively.

Ferrocyanide of potassium K₄Fe(CN)₆,3H₂O, "yellow prussiate of potash," is made by heating nitrogenous animal refuse, such as blood, with iron filings and potassium carbonate. The resulting mass contains potassium cyanide and ferrous sulphide, and when it is treated with warm water these interact and produce the ferrocyanide:

$$2KCN + FeS \rightarrow Fe(CN)_2 + K_2S,$$
$$4KCN + Fe(CN)_2 \rightarrow K_4.Fe(CN)_6.$$
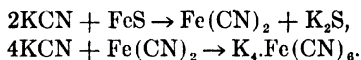
The trihydrate forms large, yellow, monosymmetric tables. Its aqueous solution contains almost exclusively the ions K+ and Fe(CN)₆⁼⁼, and gives none of the reactions of the ferrous ion Fe++. One of the double decompositions of this salt — namely, that with ferric salts — is important because it gives a gelatinous precipitate of **Prussian blue** (ferric ferrocyanide):

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4{}^{III}(Fe(CN)_6)_3{}^{IV} \downarrow + 12KCl.$$
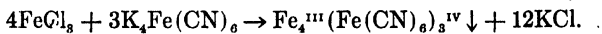
Prussian blue is employed in making paints, and is the usual pigment in laundry blueing. Although insoluble, it is such a fine powder that it appears to dissolve in the water. It is used in the laundry to correct the yellowish tint derived from the ferrous

bicarbonate in the water (p. 504). If the goods are not freed
•by rinsing from soap and soda, however, the alkali liberated by
hydrolysis of the latter enters into double decomposition with
the Prussian blue and produces more rust:

$$Fe_4(Fe(CN)_6)_3 + 12NaOH \rightarrow 4Fe(OH)_3 \downarrow + 3Na_4Fe(CN)_6.$$
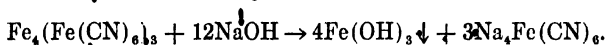
Potassium Ferricyanide $K_3{}^I[Fe(CN)_6]^{III}$. — The difference
between this and the preceding salt can be seen by writing the
formulæ thus: $4KCN,Fe(CN)_2$ and $3KCN,Fe(CN)_3$. In the
ferricyanide the iron is trivalent and the negative ion Fe (CN)$_6$≡
is also trivalent as a whole. It is a soluble salt, of red color,
made by oxidizing the ferrocyanide. With ferric salts it gives
only a brown solution, but with ferrous salts it gives a deep
blue precipitate of ferrous ferricyanide — **Turnbull's blue:**

$$3FeCl_2 + 2K_3Fe(CN)_6 \rightarrow Fe_3(Fe(CN)_6)_2 \downarrow + 6KCl.$$
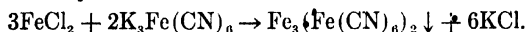
We can *distinguish ferrous-ion* Fe++ from *ferric-ion* Fe+++
by this reaction. An equally sharp distinction is obtained by
adding potassium thiocyanate, for, although the **ferrous** and
ferric thiocyanates are both soluble, the latter is *blood red* in
·color (see p. 209).

Blue-Prints. — Some ferric salts are reduced to ferrous salts
when exposed to light. Thus ferric oxalate $Fe_2(C_2O_4)_3$ will keep
in the dark, but in light gives ferrous oxalate FeC_2O_4:

$$Fe_2(C_2O_4)_3 \rightarrow 2FeC_2O_4 + 2CO_2 \uparrow .$$
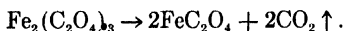
When paper is dipped in ferric oxalate solution and dried, and a
fern (or ink drawing on transparent paper) is placed over the
prepared sheet, sunlight will reduce the iron to the ferrous condi-
tion excepting where the fern or ink lines protect it from the light. ·
When the sheet is now dipped in potassium ferricyanide solution
(developer), the ferric oxalate gives only the brown substance
which can be washed out. But the parts exposed to the light
turn deep blue from the precipitation of ferrous ferricyanide in
the paper. The pattern is white on a blue ground. In regular
blue-print paper ammonium-ferric citrate takes the place of the

oxalate, and the ferricyanide has already been applied to·the paper, so that only exposure and washing remain to be done.

The student may make blue-prints for his own use as follows. Dissolve 10 g. of potassium ferricyanide in 100 c.c. of water, and 13 g. of ammonium-ferric citrate in a second 100 c.c. Mix equal volumes of the two solutions and filter if there is any precipitate. Paint evenly over the paper with a clean camel's-hair brush, dry, and keep in a dark place until required.

Ink. — Writing ink is commonly made by adding ferrous sulphate to an extract of nut-galls. The active constituent of this extract is tannic acid, useful also in dyeing (p. 591) and in tanning leather (p. 680). Tannic acid is not, strictly speaking, a single substance, but a mixture of complex phenolic acids (see p. 441). Ferrous tannate is soluble and almost colorless, but is slowly oxidized, when exposed to air, to the insoluble, black ferric tannate. To make the writing visible from the first, a blue or black dye is added to the ink.

Stains of fresh writing ink, being soluble, can usually be washed out with water, if the latter is used at once. After the oxidation has occurred, the ferric tannate must be reduced again, by soaking the part for 12 hours or longer in ammonium oxalate solution, and the ink can then be washed out. Rust stains are often rendered soluble by ammonium oxalate also.

Iron Carbonyls. — When carbon monoxide is led over finely divided iron at 40–80°, or under eight atmospheres pressure at the ordinary temperature, volatile compounds of the composition $Fe(CO)_4$, iron **tetracarbonyl**, and $Fe(CO)_5$, the **pentacarbonyl**, are formed. When the gaseous mixture is heated more strongly, the compounds decompose again, and iron is deposited. Illuminating-gas burners frequently receive a deposit of iron from this cause.

Analytical Reactions of Compounds of Iron. — There are two ionic forms of iron, ferrous-ion Fe^{++}, which is very pale-green, and ferric-ion Fe^{+++}, which is almost colorless. Ammonium sulphide gives with the former black ferrous sulphide, which is soluble in dilute acids. The hydroxides are white and brown,

respectively. With ferrocyanide of potassium, ferrous salts give a white, and ferric salts a blue precipitate. With ferricyanide of potassium the former gives a deep-blue precipitate, and the latter a brown solution. Ferric thiocyanate $Fe(CNS)_3$ is deep-red (p. 209). With borax, iron compounds give a bead which is green (ferrous borate) in the reducing flame, and colorless or, with much iron, yellow (ferric borate) or even brown when oxidized.

Cobalt Co and Nickel Ni

In olden times ores containing cobalt and nickel were frequently mistaken for iron and copper ores, and were treated accordingly. Failure to isolate the expected metals was regarded as due to supernatural influences, hence the word *cobalt* is derived from the German *Kobald,* an evil spirit (akin to the English "goblin"), while the connection between *nickel* and the chief of evil spirits is obvious. Cobalt continued to justify its name until very recently; only within the last few years have any applications of the metal been discovered. Nickel, on the other hand, has long ago found many uses.

The Chemical Relations of Cobalt. — Cobalt forms cobaltous and cobaltic oxides and hydroxides CoO and $Co(OH)_2$, Co_2O_3 and $Co(OH)_3$, respectively, which are all basic, the former more so than the latter. The cobaltous salts are little hydrolyzed, but the cobaltic salts are largely decomposed by water. The latter also liberate readily one-third of the negative radical, after the manner of manganic salts, becoming cobaltous. Complex cations and anions containing cobalt are very numerous and very stable.

Occurrence and Properties. — Cobalt is found along with nickel in smaltite $CoAs_2$ and cobaltite $CoAsS$. The pure metal may be made by Goldschmidt's process, or by reducing the oxalate, or an oxide, with hydrogen. The metal is silver-white, with a faint suggestion of pink. It displaces hydrogen slowly from dilute acids, but interacts readily with nitric acid.

An alloy of cobalt, chromium and tungsten (**stellite**) is used

for high-speed tools. When heated, it 'keeps its temper even better than the special steel alloys (p. 699).

Cobaltous Compounds. — The chloride $CoCl_2,6H_2O$ may be made by treating the oxide with hydrochloric acid. It forms red prisms, and when partially or completely dehydrated becomes deep-blue. Writing made with a diluted solution upon paper is almost invisible, but becomes blue when warmed and afterwards takes up moisture from the breath, ard'is once more invisible (**sympathetic ink**). Most cobaltous compounds are red when hydrated or in solution (Co^{++}), and blue when dehydrated. By addition of sodium hydroxide to a cobaltous salt, a blue basic salt is precipitated. When the mixture is boiled, the pink **cobaltous hydroxide** $Co(OH)_2$ is formed. This becomes brown through oxidation by the air. It interacts with ammonium hydroxide, giving a soluble ammonio-cobaltous hydroxide, which is quickly oxidized by the air to an ammonio-cobaltic compound (see below). It dissolves also in salts of ammonium as does magnesium hydroxide (p. 560). When dehydrated it leaves the black **cobaltous oxide** CoO. The black **cobaltous sulphide** CoS_c is precipitated by ammonium sulphide from solutions of all salts, and even by hydrogen sulphide from the 'acetate. A sort of **cobalt glass**, made by fusing sand, cobalt oxide, and potassium nitrate, forms, when powdered, a blue pigment, **smalt**, used in china-painting and 'oy artists.

Cobaltic Compounds. — By addition of a hypochlorite to a solution of a cobaltous salt, **cobaltic hydroxide** $Co(OH)_3$, a black powder, is precipitated. Cautious ignition of the nitrate gives **cobaltic oxide** Co_2O_3. Stronger ignition gives the commercial oxide, which is a **cobalto-cobaltic oxide** Co_3O_4. Cobaltic oxide dissolves in cold hydrochloric acid, but the solution gives off chlorine when warmed.

Complex Compounds. — Potassium cyanide precipitates from cobaltous salts 'a brownish-white cyanide. This interacts with excess of the reagent, giving a solution of **potassium cobaltocyanide** $K_4.Co(CN)_6$ (compare p. 704). This compound is easily

oxidized by chlorine, or even when the solution is boiled in the
air, and the colorless **potassium cobalticyanide** is formed:

$$4K_4Co(CN)_6 + 2H_2O + O_2 \rightarrow 4K_3.Co(CN)_6 + 4KOH.$$
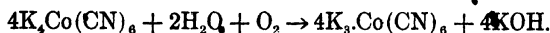
The solution gives none of the reactions of Co^{+++}, and with
acids the very stable cobalticyanic acid, $H_3Co(CN)_3$, is liberated.

When acetic acid and potassium nitrite are added to a cobalt-
ous salt, the latter is oxidized by the nitrous acid (liberated by
the acetic acid) and a white complex salt $K_3.Co(NO_2)_6$, **potassium
cobaltinitrite**, is thrown down.

Cobaltic salts give with ammonia complex compounds which
are many and various. The cations often contain negative
groups, and are such as $Co(NH_3)_6^{+++}$, $Co(NH_3)_5Cl^{++}$ and
$Co(NH_3)_5NO_2^{++}$. Usually the solutions give none of the reac-
tions of cobaltic ions, and often fail likewise to give those of
the anion of the original salt.

The Chemical Relations of Nickel. — Nickel forms nickelous
and nickelic oxides and hydroxides NiO and $Ni(OH)_2$, Ni_2O_3
and $Ni(OH)_3$, but only the former are basic. The nickelous salts
resemble the cobaltous and ferrous salts, but are not oxidizable
into corresponding nickelic compounds. Since there are no
nickelic salts, there are here no analogues of the cobalticyanides
or the cobaltinitrites. The complex nickelous salts, like the com-
plex cobaltous salts, and unlike the complex cobaltic salts, are
unstable, and so give some of the reactions of Ni^{++}.

Occurrence and Properties. — Nickel occurs free in meteor-
ites. It is now manufactured chiefly from **pentlandite** [Ni,Cu,-
Fe]S, found at Sudbury (Ontario), and from **garnierite**, a silicate
of nickel and magnesium, found in New Caledonia. In the
former case, the ore is roasted, smelted, and finally besse-
merized. The resulting alloy of copper and nickel is much used
for sheet-metal work (**Monel metal**, approx. 1 : 1). Pure nickel
is separated from the copper by an electrolytic process (p. 613),
or by the Mond process (see below).

The metal is white, with a faint tinge of yellow, is very hard,
and takes a high polish (m.-p. 1452°). It is used in making

alloys, such as German silver (copper, zinc, nickel, $2:1:1$) and the "nickel" used in coinage (copper, nickel, $3:1$). Nickel plating on iron is accomplished exactly like silver plating (p. 624). The bath contains an ammoniacal solution of ammonium-nickel sulphate $(NH_4)_2SO_4,NiSO_4,6H_2O$, and a plate of nickel forms the anode.

' The metal rusts very slowly in moist air.' It displaces hydrogen with difficulty from dilute acids, but interacts with nitric acid.

Compounds of Nickel. — The chloride $NiCl_2,6H_2O$ is made by treating any of the oxides with hydrochloric acid, and is green in color (when anhydrous, brown). The sulphate $NiSO_4,-6H_2O$ is the most familiar salt. **Nickelous hydroxide** $Ni(OH)_2$ is formed as an apple-green precipitate, and when heated leaves the green **nickelous oxide** NiO. It dissolves in ammonium hydroxide, giving a complex nickel-ammonia cation. It is soluble also in salts of ammonium (compare p. 560). By cautious ignition of the nitrate, **nickelic oxide** Ni_2O_3 is formed as a black powder. The oxides and salts, when heated strongly in oxygen, give the oxide Ni_3O_4. The last two oxides liberate chlorine when treated with hydrochloric acid, and give nickelous chloride. **Nickelic hydroxide** $Ni(OH)_3$ is a black precipitate formed when a hypochlorite is added to any salt of nickel. **Nickelous sulphide** is thrown down by ammonium sulphide, and behaves like cobaltous sulphide ' (p. 708).

Addition of **dimethylglyoxime** to an ammoniacal solution of a salt of nickel gives a brilliant scarlet precipitate of **an acid salt:**

$$Ni(OH)_2 + 2(HON)_2C_2(CH_3)_2 \rightarrow 2H_2O + NiH_2[C_2N_2O_2(CH_3)_2]_2.$$
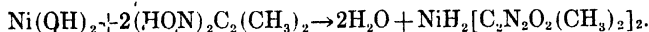
No precipitate with this organic reagent is given by salts of cobalt.

With potassium cyanide and a salt of nickel the greenish **nickelous cyanide,** $Ni(CN)_2$, is first precipitated. This dissolves in excess of the reagent, and a complex salt $K_2Ni(CN)_4,H_2O$ may be obtained from the solution. This salt is of different composition from the corresponding compounds of cobalt and of iron, and is less stable. Thus, with bleaching powder, it gives

Ni(OH)₃ as a black precipitate. When the solution is boiled in the air no oxidation to a complex nickelicyanide occurs, and indeed no such salts are known. This fact enables the chemist to separate cobalt and nickel, for when the mixed cyanides are boiled and then treated with bleaching powder, the cobalticyanide is unaffected. With potassium nitrite and acetic acid no insoluble compound corresponding to that given by cobalt salts is formed by salts of nickel. This action also is used for the purpose of separation.

When finely divided nickel, made by reducing the oxide or oxalate with hydrogen at a moderate temperature, is exposed to a stream of cold carbon monoxide, nickel carbonyl $Ni(CO)_4$ is formed. This is a vapor and is condensable to a colorless liquid (b.-p. 43° and m.-p. –25°). The vapor is poisonous. When heated to 150–180° it is dissociated and nickel is deposited. Cobalt forms no corresponding compound. Commercially, pure nickel is separated from copper (and cobalt) in the **Mond process** by passing carbon monoxide over the pulverized alloy, and subsequently heating the gas.

Analytical Reactions of Compounds of Cobalt and Nickel. — The cobalt ion Co^{++} is pink, and the nickelous ion Ni^{++} green. The reactions used in analysis have been described in the preceding paragraphs. With borax, cobalt compounds give a blue bead (cobaltous borate), and nickel compounds a bead which is brown in the oxidizing flame and cloudy, from the presence of gray, metallic nickel, when reduced.

Exercises. — 1. What would be the interactions of calcium carbonate when fused with sand and with clay, respectively?

2. Make equations representing, (a) the oxidation of ferrous chloride by air, (b) the hydrolysis of ferrous carbonate and the oxidation of ferrous hydroxide, (c) the oxidation of ferrous sulphate in the presence of sulphuric acid by hypochlorous acid, (d) the reduction of ferric chloride by iron and by hydrogen sulphide, respectively, (e) the formation of ferric ferrocyanide and of ferrous ferricyanide.

3. Explain the solubility of cobaltous and nickelous hydroxide in salts of ammonium.

4. Construct equations to show the formation, (a) of the insoluble potassium cobaltinitrite (nitric oxide is given off), (b) of nickelic hydroxide from nickelous chloride and sodium hypochlorite. Remembering that the hypochlorite is somewhat hydrolyzed, explain why the precipitation in (b) is complete.

5. Tabulate in detail the chemical relations of the elements cobalt and nickel, with especial reference to showing the resemblances and differences.

6. How could you demonstrate that ferric hydroxide is in colloidal suspension in water, and not dissolved?

CHAPTER L

As in Chapter XXXII, so here, we assume that the specimen to be identified contains a single substance. We consider first the metallic elements, and limit ourselves to those that have been described in the context. Our review will cover, mainly, the properties of each simple metallic positive radical.

External Examination. — The color is often significant. Most of the common compounds of iron, nickel, cobalt, copper, gold, manganese and chromium are colored (see text). A metallic luster (scrape off the tarnish) usually, though not always, indicates a free metal or an alloy. The crystalline form should be noted. The odor usually gives information about non-metallic constituents (p. 460) only. As regards state, the vast majority of the metals and their compounds are solids. When a liquid presents itself, therefore, it is usually an aqueous solution of some compound. Obtain the solid by evaporation.

Solubility and Reaction of the Solution. — Ascertain whether the substance is soluble in water (table on inside front cover). Note whether the solution is acid, alkaline, or neutral in reaction (p. 469). No substance can be identified by the preceding observations alone, but the final conclusion as to the nature of the specimen must be in harmony with them.

A salt which gives an acid reaction must be an acid salt of a polybasic acid (p. 247), or a derivative of a strong acid and a weak base. Similarly a salt which reacts alkaline must be a *basic* salt, or a derivative of a weak acid and a strong base.

Recognition by Reactions in Solution. — Starting with the substance in solution, its identity can be ascertained by using

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reactions involving mainly precipitations and oxidations or .re-
ductions, which separate the metals into five distinct groups.

The following plan, taken in conjunction with the statements
in the context, shows how a *single* *cation* may be identified.
What will be said applies only to the case of a solution con-
taining salts like the chlorides, nitrates, or sulphates, of one or
more cations, and leaves the oxalates, phosphates, cyanides, and
some other salts out of consideration.

Before attempting to understand this plan, the student should
turn to the discussion, on *ionic equilibria* (Chapter XL) and read
it carefully through. The sections on the *solubility of precipi-
tates* (pp. 572-578) should be particularly studied, since upon
the principles therein formulated the whole plan is directly based.*

Group I. — Add to the solution hydrochloric acid. A pre-
cipitate indicates that cations giving insoluble chlorides are
present. Silver, mercurous and lead salts give the white $AgCl$,
$HgCl$, and $PbCl_2$ respectively. The last-named salt, being ap-
preciably soluble, will be only incompletely precipitated.

These three chlorides can be distinguished from one another
very easily. When excess of ammonium hydroxide is added to
the precipitate, *silver chloride dissolves* (p. 622). *Mercurous*
chloride turns black, owing to the formation of a finely divided
mixture of free mercury and mercuric amidochloride $Hg(NH_2)Cl$.
Lead chloride remains apparently *unchanged.*

Group II. — If no precipitate appears on addition of hydro-
chloric acid, hydrogen sulphide is led into the solution. The sul-
phides insoluble in active acids, namely, HgS, CuS, PbS, Bi_2S_3,
CdS, As_2S_3, Sb_2S_3, SnS, are therefore thrown down. The first
four are black or dark brown, the next two are yellow, and the
last two are orange and brown respectively. If too much HCl
is present, the precipitation of several of these sulphides will be
incomplete. On the other hand, if too little HCl is used, zinc
sulphide may be partially precipitated (see pp. 573-575).

* Many experimental details, essential for the successful performance of
the tests described in this chapter, are here omitted. They will be found
in the Author's *Laboratory Outline of College Chemistry.*

.This group is readily *sub-divided.* The last three sulphides pass into solution when warmed with yellow ammonium sulphide, for they give soluble *complex sulphides.* The first five sulphides will be unaffected.

Group IIa. — HgS, CuS, PbS, Bi_2S_3, CdS. A *yellow* precipitate insoluble in ammonium sulphide indicates *cadmium.* To distinguish between the remaining four sulphides, boil with HNO_3; *HgS* alone does *not* go into solution. Dilute the solution, and add H_2SO_4. *Lead* gives a *white precipitate* of $PbSO_4$. If no precipitate is obtained, add NH_4OH till alkaline. *Bismuth* gives a *white precipitate* of $Bi(OH)_3$, *copper* a *blue solution.*

Group IIb. — As_2S_3, Sb_2S_3, SnS. The color distinction is not always certain. Reprecipitate the sulphides by adding HCl, and boil the precipitate with concentrated HCl. As_2S_3 does *not* dissolve. If the precipitate does dissolve, cool the solution and place in it a piece of bright tin. A *black deposit* forming on the surface (by displacement, see p. 240) indicates Sb.

Group IIIa. — If no precipitate is obtained with H_2S, the solution is boiled, and a few drops of concentrated HNO_3 added to oxidize any *ferrous* salt to the *ferric* state. Ammonium chloride is added, and then ammonium hydroxide *in excess.* A *white, gelatinous* precipitate of $Al(OH)_3$ indicates *aluminium,* a *bluish-green* precipitate of $Cr(OH)_3$ indicates *chromium,* a *reddish-brown* precipitate of $Fe(OH)_3$ indicates *iron.* The presence of NH_4Cl is necessary to reduce the concentration of OH^- furnished by the NH_4OH below the point at which other less insoluble hydroxides (such as $Mn(OH)_2$) would be precipitated. To tell whether iron was originally present in the ferrous or the ferric condition, the *ferricyanide test* (p. 705) should be applied.

Group IIIb. — If, still, no precipitate is obtained, hydrogen sulphide is led into the *alkaline* solution. Sulphides which are insoluble in water, but soluble in active acids (see pp. 329, 578), now appear. They are CoS and NiS (both black), MnS (flesh-colored) and ZnS (white). To distinguish between Co and Ni, add NaOH to the original solution. *Cobalt* gives a *blue* precipitate of a basic salt, changing to *pink* $Co(OH)_2$ on boiling; *nickel* gives a *light-green* precipitate of $Ni(OH)_2$.

Group IV. — If negative results are still obtained, add $(NH_4)_2CO_3$. A white precipitate is given by three of the remaining metals whose carbonates are insoluble, *calcium, strontium* and *barium*. Distinction between these three may be made by the *flame test*. A small portion of the precipitate is taken up on a platinum wire and held in the Bunsen flame. A *brick-red* coloration signifies Ca, a *crimson-red* Sr, a *green* Ba.

Group V. — The only other common positive radicals are Mg, NH_4, K and Na. On addition of ammonium phosphate to the solution from Group IV, *magnesium*, if present, is precipitated in the form NH_4MgPO_4 (white). An ammonium salt may be recognized by boiling some of the original solution with $NaOH$, when *ammonia* is evolved. *Potassium* salts confer a *violet* coloration to the Bunsen flame; *sodium* salts a *bright yellow*.

Confirmatory Tests. — From the context in earlier chapters, the student will be able to pick out for each particular metal other tests which may serve to confirm the conclusions arrived at in the course of the above analysis. Often the metallic radical can be recognized by a *displacement* reaction (compare pp. 612, 618). Often, again, *color changes* which occur during the course of the scheme of operations outlined above give indications of value. Thus a *yellow* solution changing to *green* during the passage of H_2S in Group II signifies a chromate (p. 679), a *purple* solution becoming *colorless* signifies a permanganate (p. 689). The borax and microcosmic salt bead colorations (see pp. 456, 413) also supply exceedingly valuable confirmatory evidence in many cases.

Tests for Negative Radicals. — Precipitation reactions similar in nature to those outlined above may be utilized as additional tests for the negative radical of an unknown substance (see Chapter XXXII). Thus a *chloride* gives with *silver nitrate* a *white* precipitate, soluble in ammonia. A *sulphate* gives a *white* precipitate with *barium chloride*, insoluble in hydrochloric acid. From the context, the student will be able to discover for himself confirmatory tests of this kind for most of the common

negative radicals discussed in this book. For a complete scheme, however, a manual of qualitative analysis should be consulted.

Insoluble Substances.— If the unknown substance is insoluble in water, try to bring it into solution by boiling successively with dilute HNO_3, concentrated HNO_3, and *aqua regia* (p. 398). In case it dissolves, evaporate off the excess of acid and proceed with the analysis as above. The only common substances which are still *insoluble* are the sulphates of Pb, Sr, Ba; certain mineral oxides such as Al_2O_3, Cr_2O_3, Fe_2O_3, SnO_2; some silicates; CaF_2; AgCl (soluble in NH_4OH). Fuse with Na_2CO_3 in a crucible, cool, extract with water, and filter.

The *residue* contains the *positive radical* as carbonate, and may be analyzed for this after dissolving in HNO_3. The *filtrate* contains the *negative radical* as sodium salt, and may be examined as in Chapter XXXII.

Exercises. — 1. Name some substances that have a metallic luster, but are not metals or alloys.

2. Name the metals whose salts with active acids will give: (*a*) neutral aqueous solutions; (*b*) acid aqueous solutions. What classes of salts will give alkaline solutions?

3. Write full ionic equations for the chloride precipitations mentioned in Group I. Why is silver chloride soluble in ammonia?

4. Write full ionic equations for the sulphide precipitations mentioned in Group II. Which is the more soluble in water, mercuric sulphide or cadmium sulphide?

5. Write full ionic equations for the hydroxide precipitations mentioned in Group IIIa. Which is the more soluble in water, aluminium hydroxide or magnesium hydroxide?

6. Write full ionic equations for the sulphide precipitations mentioned in Group IIIb. Which is the more soluble in water, nickel sulphide or zinc sulphide?

7. Write full ionic equations for the carbonate precipitations mentioned in Group IV.

8. Write full ionic equations for the reactions mentioned in Group V.

9. Give a precipitation test for the negative radical in each of the following substances: sodium hydroxide, potassium carbonate, sodium sulphide, sodium phosphate. Write full ionic equations in each case.

10. Tabulate the metals which could be identified by means of borax bead tests, naming the compound formed and its color in each case.

CHAPTER LI

IN this concluding chapter an effort is made to indicate some of the more significant recent advances in our knowledge of the fundamental principles of chemistry. The topics taken up are presented in the briefest possible outline, and it is not expected that the beginner will derive, from these pages alone, anything more than a general idea of the trend of modern chemical theory. How revolutionary this has become may be recognized by the jocular proposal that the Atom (Greek, a- not, -tom divided; see p. 99) be now re-christened "Tom" to celebrate its dismemberment.

Fascinating as the results of recent work may appear, the reader should not lose sight of the fact that, for all practical purposes and in the chemistry of daily life, the immutability of elements, the constancy of atomic weights, and the law of definite proportions may still be accepted and utilized without any reservations. The subject of greatest importance in this chapter, from the student's standpoint, is the correlation of **valence and atomic structure.**

The Discovery of Radium. — In 1896 Henri Becquerel discovered that a crystal of a salt of uranium could, in the dark, reduce the silver bromide on a photographic plate, even when a sheet of black paper (impervious to light) was placed between. Evidently a *radiation,* different from light, was given out by the salt. Next he discovered that an electrometer (Fig. 141), in which the gold leaves had been caused to separate by charging with electricity, lost its charge rapidly when a salt of uranium was brought near to the knob connected with the leaves. Evidently the salt *rendered the air a conductor* ("ionized"

FIG. 141.

719
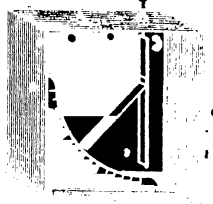
;he air), and this permitted the escape of the electricity. These discoveries, in the hands of a multitude of observers, have led to the development of an entirely new branch of our science, namely **radio-chemistry.**

The radioactivity of every pure uranium compound is proportional to its uranium content. The ores are, however, relatively four times as active. This fact led M. and Mme. Curie, just after 1896, to the discovery that the pitchblende residues, from which practically all of the uranum had been extracted, were nevertheless quite active. About a ton of the very complex residues having been separated laboriously into the components, it was found that a large part of the radioactivity remained with the sulphate of barium. From this a product free from barium, and at least one million times more active than uranium, was finally secured in the form of the bromide. The nature of the spectrum and the chemical relations of the element, now named **radium,** placed it with the metals of the alkaline earths. The ratio by weight of chlorine to radium in the chloride is 35.46 : 113, so that, on the assumption that the element is bivalent, its chloride is $RaCl_2$ and its atomic weight is 226. With this value it occupies a place formerly vacant in the periodic table.

In 1910 Mme. Curie obtained metallic radium by electrolyzing a solution of radium chloride, using a mercury cathode, and expelling the mercury by distillation. It was a white metal (m.-p. 700°) which, like calcium, quickly tarnished in the air and displaced hydrogen from water.

The Nature of the "Rays." — Many properties show that the "rays" emitted by compounds of uranium and of radium are of three kinds. They are most sharply distinguished from one another when allowed to pass through a powerful magnetic field. The **alpha-rays** are positively charged and are bent in one direction while the **beta-rays** are negative and are bent in the other. The **gamma-rays** are not affected.

The *alpha-rays* are **atoms of helium** (p. 376) thrown off in straight lines with varying initial velocities, averaging about

1

2

3

4
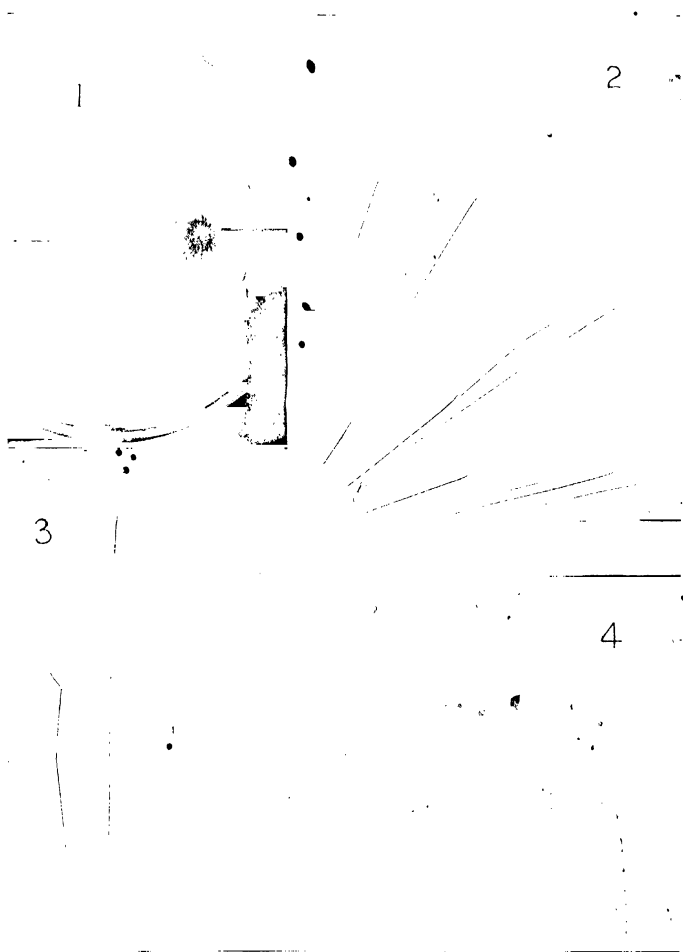
FOG-TRACKS FROM RADIUM (C. T. R. WILSON)

1. 2. Paths of helium atoms.   3. Part of 2, enlarged.   4. Paths of electrons.

one-tenth that of light. Each such atom bears a **double positive charge** (in other words, it has *lost two electrons*, see p. 267), and a delicate electrometer readily indicates the impact of a single atom. These alpha-particles, being each four times as heavy as an atom of hydrogen, plough their way through tens of thousands of air-molecules and usually go about 3–8 cm. before being stopped. The emission of atoms of helium can be detected by means of Crookes' spintharoscope (Fig. 142). The particle of radium bromide is at *B*, and some of the charged helium-atoms strike a surface *C* covered with zinc sulphide, producing faint flashes of light. The lens *A* magnifies the flashes, which can be seen in a dark room after the eye has become thoroughly rested (15–20 minutes). The helium gas given off by radium compounds was collected by Soddy working with Ramsay and identified, and its rate of production was measured. The amount was equal to 158 cubic mm. per 1 g. of radium per year.
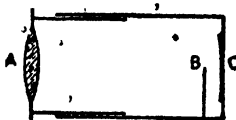
Fig. 142.

The *beta-particles* are **electrons** (p. 266), or unit charges of negative electricity, and are shot out with a velocity approaching that of light (300,000 kiloms. per sec.). Their apparent mass is very small (about $\frac{1}{1830}$ that of an atom of hydrogen). Owing to collisions with the relatively ponderous air-molecules, half of them are lost after going about 4 cm.

The *gamma-rays* are identical with X-rays (see p. *120*), and are presumably produced like the latter by the impacts of the electrons on the surrounding matter.

The helium atoms are almost all stopped by a sheet of paper or by aluminium foil 0.1 mm. thick. The electrons have greater penetrating power, many passing through gold-leaf, but being practically all blocked by a sheet of aluminium 1 cm. thick. The gamma-rays (X-rays), however, are able to penetrate relatively thick layers of metals and other materials of low atomic weight.

One of the most striking facts is that the stoppage by the air

of so many rapidly moving particles results in the production of much *heat*. One gram of radium would produce about 120 calories per hour.

Disintegration. — The emission of atoms of helium and of electrons was first explained by Rutherford (1902-3), then of McGill University, Montreal, as being due to the spontaneous **disintegration of the atoms of uranium, radium, and other radioactive elements** This, Rutherford was the first to show that radium compounds produced a gaseous substance called the radium emanation (niton), which was the residue left after the emission of one atom of helium from an atom of radium. This gas was itself radioactive and underwent further disintegration, depositing a solid radioactive residue on bodies in contact with it. Furthermore, every known uranium ore contains radium (McCoy) and radium emanation (Boltwood) in amounts proportional to the uranium content. Also, after the radium has been removed, the pure uranium compound gives off at first only -particles, but gradually recovers its whole radioactivity and is then found to contain radium emanation once more (Soddy). t thus appears that uranium is the starting point, and that the disintegration proceeds by steps, producing a number of different products. Each of these is formed from one such product and by disintegration furnishes another.

Unlike ordinary chemical change, the rate of disintegration is not affected by conditions. It can neither be started nor stopped at will. It is no more vigorous at 2000° than at −200°. Other changes occur between atoms, these within each atom.

The law, due also to Rutherford, describing the rate at which any one radioactive element disintegrates is simple. Only a certain fraction of the whole of any one specimen undergoes the change in unit time. Thus, as the total amount diminishes because of the change, the amount changing during the next unit of time, being a constant fraction of the whole, must be less. Hence an infinite time would be required for the complete disintegration of any one specimen. For convenience in expressing the rate of disintegration, however, we calculate and tabulate the **average life** of the element.

Radium emits helium atoms at the rate of 3.4×10^{10} per gram per second. From this fact, we can calculate its average life to be about 2400 years. Hence, if it were not continuously being produced (from uranium), the whole supply would have been exhausted long before the earth reached a habitable condition.

The Uranium Group of Radioactive Elements. — The following shows the various elements produced from uranium by successive disintegrations. When a helium atom, or an electron is expelled, the fact is shown by the symbols He and ε, respectively. The first number below each element is the average life of that member of the series (y = year, d = day, h = hour, m = minute, s = second). The second number is the atomic weight, obtained by subtracting from the at. wt. of uranium (238) the weight (4) of each helium atom emitted.

U_1 $\rightarrow$ He + U-X$_1$ $\rightarrow$ ε + U-X$_2$ $\rightarrow$ ε + U$_2$ $\leftrightarrow$ He + Ionium
8×10^9 y. 35.5 d. 1.65 m. 3×10^5 y. 2×10^5 y.
238 234 234 234 230

$\rightarrow$ He + Ra $\rightarrow$ He + Niton $\rightarrow$ He + Ra-A $\rightarrow$ He + Ra-B
2440 y. 5.55 d. 4.3 m. 38.5 m.
226 •222 218 214

$\rightarrow$ ε + Ra-C $\rightarrow$ ε + Ra-C$_1$ $\rightarrow$ He + Ra-D $\rightarrow$ ε + Ra-E
28.1 m. 10^{-6} s. 24 y. 4.2 d.
214 214 210 210

$\rightarrow$ ε + Ra-F $\rightarrow$ He + Pb (end)
196 d.
210 206
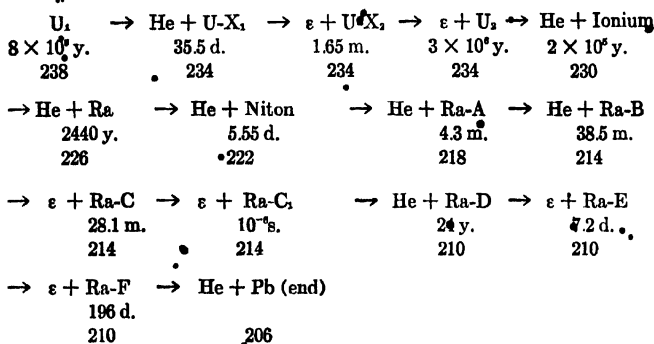
The radium emanation was shown by Ramsay to be one of the inert gases (p. 377), and was renamed niton. Its density was determined experimentally with a small sample, using a micro-balance capable of weighing 1/500,000 mgm., and found to be 222.4 (density of oxygen = 32).

The end-product of the disintegration is lead, and all uranium ores contain lead (see p. 727).

Thorium, found as phosphate in monazite sand, is also radioactive and furnishes a similar series of disintegration products. The final material is again lead.

Actinium and polonium are other radioactive elements, which have not yet been fully investigated.

Transmutation of Elements; Atomic Energy. — The phenomena of radioactivity establish the transmutation of elements, long regarded as a delusion of the alchemists, as an indisputable fact. It is true that we have not yet discovered any simple means of disintegrating the more common elements (see, however, the recent work of Rutherford, p. 21). We cannot even control in any way the *rate* of disintegration of radioactive elements (see p. 722). If, however, some method of inducing or hastening radioactive changes on a large scale is devised in the future, a wonderful new source of power will be put into our hands, namely, **atomic energy.**

The energy change in radioactive disintegrations is enormously greater than in ordinary chemical reactions. One gram of radium, as already mentioned, would evolve about 120 cal. per hour, and would continue to evolve this heat, at a gradually decreasing rate, for centuries. The total heat available would be over 2,000,000,000 cals. per gram, whereas a gram of carbon burning to CO_2 gives only 8040 cals. The disintegration of a pound of uranium salts would furnish enough power to drive an ocean liner across the Atlantic, but 8,000,000,000 years is entirely too long to wait for the completion of the trip. Chemists are already looking forward, however, to the possibility of using the enormous stores of energy here available so soon as a *catalyst* for the reaction is obtained.

Another interesting by-product of this subject is the calculation that the heat given off by the disintegration of the radium known to exist in the earth (niton is found in the soil and in well waters) is sufficient *alone* amply to account for the maintenance cf its temperature. A globe the size of the earth, possessing originally only heat energy, and cooling from a white-hot condition to the temperature of interstellar space, would have passed through the stage of habitable temperatures in a much shorter time than that which geological deposits and fossils show to have been actually available. The discovery of the enormous, but gradually released, disintegration energy of radium, enables us

now to explain the prolonged period during which life has existed in the earth.

This energy is derived *from within the atom itself,* by re-arrangements of the *protons* and *electrons* of which it is constructed (see p. 266). Building up a more complex atom from its disintegration products would require just as much energy as is evolved in the disintegration. This is another step which remains for the future.

We may now proceed to examine more intimately the question of **atomic structure,** already discussed in brief in earlier chapters (pp. 266-267).

Atomic Numbers. — Visible light, X-rays, and wireless electric waves are all vibrations of the same nature in the ether. They differ only in wave-length, the order of the wave-lengths being 10^{-5} cm., 10^{-8} cm., and 10^{6} cm. (10 kilometers), respectively. Now, just as the spectrum of visible light is obtained by using a grating, on which the rulings are separated by distances of the order of the wave-length of such light, so ordinary crystals give spectra of X-rays, because they are composed of particles arranged in rows about one thousand times closer and so form a suitable grating for X-rays. This fact was first discovered by Dr. Laue of the University of Zurich (1912). The X-rays are produced in an evacuated tube by cathode

FIG. 143.

rays, which are streams of electrons emanating from the cathode (C, Fig. 143), when they strike the anticathode (A).

With different elements on the anti-cathode, X-rays of slightly different wave-lengths, and therefore giving different X-ray spectra, are produced. The greater the number of free protons (unit positive charges) in the nucleus of the atom, the shorter should be the wave-length of the characteristic X-rays. It was shown by Moseley (a brilliant young English physicist, killed at Gallipoli) that when the elements are arranged in the order of these wave-lengths, whole numbers can be assigned to each which are inversely proportional to the wave-lengths of

corresponding lines in their X-ray spectra. These **atomic num-bers** have been determined for most of the elements; the atomic weights of which lie between those of aluminium and uranium. In the following table, the atomic numbers for these elements are given and, for the sake of greater completeness, numbers for the twelve elements preceding Al have been inserted also.

ATOMIC NUMBERS (MOSELEY)

H 1	He 2	Li 3	Gl 4	B 5	C 6	N 7	O 8	F 9	......	......	......
......	Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	......	......	......
......	A 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28
......	......	Cu 29	Zn 30	Ga 31	Ge 32	Ar 33	Se 34	Br 35	......	......	......
......	Kr 36	Rb 37	Sr 38	Y 39	Zr 40	Cb 41	Mo 42	— 43	Ru 44	Rh 45	Pd 46
......	......	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	......	......	......
......	Xe 54	Cs 55	Ba 56	La 57	Ce 58	Ta 73*	W 74	— 75	Os 76	Ir 77	Pt 78
......	......	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	......	......	......
......	Nt 86	— 87	Ra 88	Ac 89	Th 90	U-X₂91	U 92	......	......	......	......

* The atomic numbers 59-72 are those of the metals of the rare earths: Pr 59, Nd 60, — 61, Sa 62, Eu 63, Gd 64, Tb 65, Dy 66, Ho 67, Er 68, Tm 69, Yb 70, Lu 71, Hf (Hafnium, discovered 1923) **72.**

It will be seen that there is a whole number available for every known element, up to and including uranium, and not omitting the rare earths which have no satisfactory place in the periodic system. There are five blank numbers in the table, which correspond to three spaces in the eighth column periodic system, one in the second column, and one more amongst the rare earths, indicating only five elements with atomic weights less than that of uranium yet to be discovered. The atomic numbers of argon and potassium place them in the chemically correct order, while the atomic weights do not. The same is true of cobalt and nickel and of tellurium and iodine.

The atomic numbers represent the number of free positive charges of electricity in the nucleus of the atom of each element. It must be noted that the nucleus also contains, in all cases except hydrogen, a number of *bound* positive charges associated with an equal number of electrons, indicated by the difference between the atomic weight and the atomic number.

The atomic numbers apparently determine all the properties of each element, and are more fundamental than the atomic

weights. The latter are secondary properties, in most cases modified by other factors, and in a few cases actually thrown out of order by such factors.

Atomic Numbers of Radioactive Elements; Isotopes. — When an atom of a radioactive element loses an atom of helium, it also loses two free positive charges from its nucleus. Its atomic number is consequently reduced by two (for example, Radium = 88, Niton = 86). When, on the other hand, a radioactive change takes place involving the loss of an electron, a positive charge in the nucleus, previously bound, becomes free, and the atomic number is found to be increased by one.

With these facts in mind, an examination of the uranium disintegration series discloses that several elements (for example, Radium – B, Radium – D, Radium – G and Lead) must exist which possess the same atomic numbers, but different atomic weights. Such elements are known as isotopes.• Isotopes are identical in all of their chemical properties, although they differ in atomic mass (see p. 23). This shows conclusively that atomic weight is not a fundamental property, but atomic number.

Ordinary lead chloride contains the elements lead and chlorine combined in the following proportions by weight:

Lead (207.20) + Chlorine (70.92) → Lead chloride (278.12).

Richards, however, has found that the lead contained in uranium ores gives a chloride in which as little as 206.1 parts by weight of lead may be combined with 70.92 parts of chlorine, while Soddy has shown that the lead extracted from thorium ores gives a chloride which contains as much as 208.4 parts by weight of lead to 70.92 parts of chlorine. We have, therefore, three lead chlorides, all possessing the same specific properties, and being therefore the same substance, yet differing in composition. Other cases of a similar nature undoubtedly exist, although not yet encountered in actual practice.

Isotopes of Common Elements. — It has recently been shown by Aston that many common elements also are isotopic, or con-

tain *chemically identical* atoms of different weight. The method
employed by Aston was that of *positive ray analysis* (Fig. 144).
The positive rays from a discharge tube are sorted out into a
thin ribbon by means of the two parallel slits S_1 and S_2, and are
then passed between the oppositely charged plates P_1 and P_2.
The rays are deflected towards the negative plate P_2, and are
spread out into an electric spectrum. A portion of this spectrum
deflected through a given angle is selected by the diaphragm D
and passed between the circular poles of a powerful electromag-
net O, the field of which is such as to bend the rays back again
to fall on a photographic plate placed as shown. If all the rays
with a single charge have the same mass, they will converge to a
focus at F. If, however, the rays are derived from an element
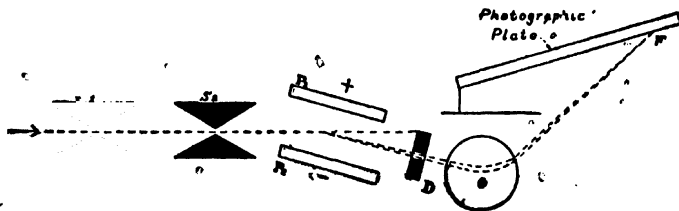
Fɪɢ. 144.

which consists of a mixture of isotopes, each isotope is distin-
guished by a separate band on the photographic plate, and from
the relative position of each band the mass of the atom to which
it corresponds can be obtained.

Chlorine (at. wt., 35.46), examined in this way, showed itself
to be a mixture of two isotopes with atomic weights *exactly* 35
and *exactly* 37. **Bromine** (at. wt., 79.92) gives isotopes with
atomic weights *exactly* 79 and *exactly* 81. **Mercury** (at. wt.,
200.6) appears to exist in as many as six forms, with atomic
weights ranging from 197 to 204. **Tin** (at. wt., 118.7) is a mix-
ture of no fewer than eight isotopes, with atomic weights 116,
117, 118, 119, 120, 121, 122 and 124! Other elements, however,
such as oxygen, nitrogen, and iodine, give no indications of
isotopes.

The fundamental atomic weights obtained by Aston are with

one exception whole numbers within the limits of experimental error. The single exception is hydrogen (at. wt., 1.008).

Atomic Structure. — On the basis of the above results, general theories of atomic structure have been built up by Harkins and Rutherford, postulating *hydrogen* and *helium atoms* as the "bricks" building up the atoms of all elements. The elements with atomic weights divisible by 4 are considered as constructed entirely of charged helium nuclei, with surrounding electrons; thus $C = 3He^{++} + 6\varepsilon$, $O = 4He^{++} + 8\varepsilon$, etc. Other elements must be assumed to contain hydrogen atoms also in their structure (see p. 21). The decrease in the mass of the hydrogen atom from 1.008 in hydrogen itself to exactly 1 in all other atomic types has been ascribed to a "**packing effect.**"

Valence and Atomic Structure. — The electrons surrounding the nucleus are arranged, according to a theory recently developed by Lewis and Langmuir, in successive concentric shells. The *total number of electrons in these shells* must be equal, since the atom as a whole is electrically neutral, to the *number of free protons in the nucleus*, in other words to the *atomic number*.

The case of the **hydrogen** atom (atomic number $= 1$) has already been considered (p. 266). The **helium** atom (atomic number $= 2$) has two electrons, which are supposed to be situated on opposite sides of the nucleus — a very stable arrangement.

No more electrons can be contained in the first shell, hence in succeeding elements the additional electrons begin to build up a *second* outer shell. Only the electrons in this outer shell can be added to or lost in interactions with other atoms (see p. 267), and it is found that, for all of the next 8 elements from **lithium** to **neon**, the tendency is either to lose electrons until none is left, or to gain electrons until a stable ring of 8 is formed. The arrangement of the electrons in this second shell has been pictured by Lewis as shown in Fig. 145. The electrons are assumed to occupy the corners of an imaginary cube, in the center of which is the atomic nucleus.

. The valence of any one of these elements is therefore repre-

sented either by the number of electrons that can be lost (**positive valence**) or by the number required to form a stable ring of 8 (**negative valence**). The next eight elements (sodium to argon)

Li   Be   B   C

N   O   F   Ne
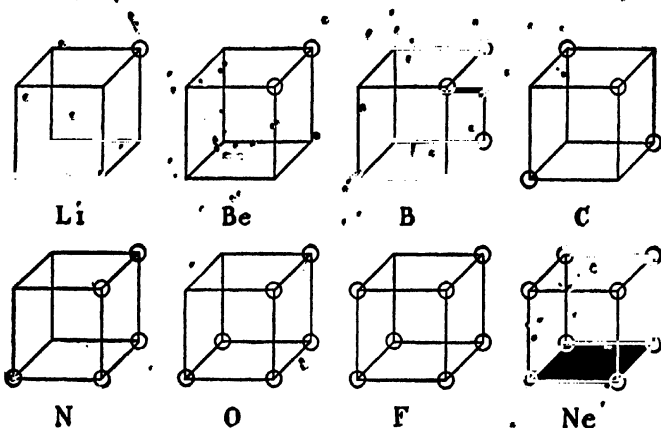
Fig. 145.

exhibit the same behavior. We have not the space here to discuss in detail the electron arrangement in these and later elements. It will suffice to mention that not only are all of the relationships suggested by the Periodic System (Chapter XXIV) confirmed, but many of the points of difficulty in Mendelejeff's tabulation are satisfactorily explained.

Li+   F-.
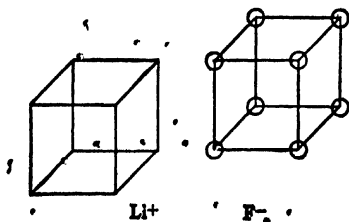
Fig. 146.

Co-Valence. — When combination takes place between two atoms (*e.g.*, Li and F) by loss and gain of electrons, we are left with a *compound*, such as **LiF** (Fig. 146), in which the constituent atoms are *apparently separate*, being held together only by the attraction of their opposite charges. An atom may also complete its stable ring of eight, however, by *sharing electrons* with another atom,

Irving Langmuir.

Gilbert N. Lewis.

as in the case of the fluorine molecule F_2 (Fig. 147). Similarly in carbon tetrachloride CCl_4, we may assume that all five atoms have completed their "octets," each chlorine atom holding a pair of electrons in common with the central carbon atom.

The number of pairs of electrons which an atom of an element can thus share with other atoms is called its **co-valence.**

F_2
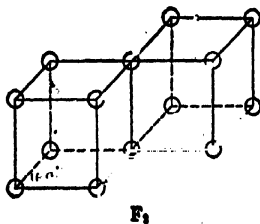
Fɪɢ. 147.

Polar and Non-Polar Compounds. — Compounds like LiF or NaCl, in which an electron has already passed from one atom to another, are evidently *potentially ionized*, and if we can diminish the attractive forces between the two charged atoms sufficiently to enable them to break away from one another, we obtain immediately the free ions (as in aqueous solution). Such compounds are termed **polar.** In substances like CCl_4, on the other hand, where electrons are held in common, the molecule will not tend to break up in this way. Such substances do not, consequently, ionize in solution, and are termed **non-polar.**

Strictly speaking, however, the distinction between *polar* and *non-polar* substances is not fundamental, but one of degree only. In no *non-polar* compound, probably, are pairs of electrons held in common so impartially that they will not tend, to some (albeit very small) extent, to pass over to one atom rather than to the other. In the same way, in no *polar* compound has the electron passed from one atom to another *completely;* the attractive forces between the two atoms, tending to restore it to its original position, must induce *some* distortion of the cubical arrangement.

Atomic Structure and Chemical Affinity. — In cases where combination between two elements produces a compound (*e.g.,* LiF) in which the arrangement of electrons is much more stable than in the original substances, we shall clearly obtain a considerable diminution in the internal energy of the system (see

pp. 199-201) as the result of the interaction. Chemical activity or affinity hence appears to depend, finally, upon atomic structure Where the electron arrangement is extremely stable, as with the helium family, the element will be *inert*. Where electrons are readily gained or lost, as with the halogens or the alkali metals the element will be *active*, and will form very stable compounds with such elements as assist most readily in the interchange.

Chemistry "within the atom" is still in its infancy, but i cannot be doubted that its development will lead to results o the greatest importance in the near future. The facts presented in this volume were almost all derived on a purely *experimenta* basis, and the construction of hypotheses to correlate and explair these facts has been a long and painful process. On the basis of atomic structure, however, the next generation of chemists wil be able to *predict* physical and chemical properties in advance A multitude of new facts will thus be brought to light, and many new applications of chemistry to industry will become evident

Exercises. — 1. What justification has been obtained in thi chapter for the use of $O = 16$ rather than $H = 1$ as a basis fo atomic weights?

2. If there are two isotopes of chlorine, and six of mercury how many varieties of mercuric chloride $HgCl_2$ are possible In what respects would these varieties be different? In wha respects would they be identical?

3. Draw diagrams showing the electron arrangements in th following molecules: hydrogen fluoride, water, oxygen (O_2), ca bon dioxide, sodium chloride.

4. Why is phosphorus quinquivalent with respect to oxyge but only trivalent with respect to hydrogen?

5. Suggest a reason why Rutherford (p. 21) failed to obta hydrogen from carbon and oxygen, while succeeding with boro nitrogen and fluorine.

6. What physical properties, discussed in this book, could utilized for the separation of chlorine into its two isotopes?

APPENDIX

I. The Metric System

Length. 1 meter (1 m.) = 10 decimeters = 100 centimeters (100 cm.) = 1000 millimeters (1000 mm.).

1 kilometer = 1000 meters (1000 m.) = 0.6214 mile.
1 decimeter = 0.1 m. = 10 centimeters = 3.937 inches.
1 meter = 1.094 yards = 3.286 ft. = 39.37 in.

Volume. 1 liter = 1000 cubic centimeters (1000 c.c.) = a cube 10 cm. × 10 cm. × 10 cm.
1 liter = 0.03532 cu. ft. = 61.03 cu. in. = 1.057 quarts (U. S.) or 1.136 quarts (Brit.) = 34.1 fl. oz. (U. S.) = 35.3 oz. (Brit.).

1 fluid ounce (U. S.) = 29.57 c.c. 1 ounce (Brit.) = 28.4 c.c.
1 cu. ft. = 28.32 liters.

Weight. 1 gram (g.) = wt. of 1 c.c. of water at 4° C. 1 kilogram = 1000 g.
1 gram = 10 decigrams = 100 centigrams (100 cgm.) = 1000 milligrams (1000 mgm.).

1 kilogram = 2.205 lbs. avoird. (U. S. and Brit.).
1000 kilograms = 2205 lbs. = 1 metric ton.
1 lb. avoird. = 453.6 g.
1 oz. avoird. (U. S. and Brit.) = 28.35 g. 100 g. = 3.5 oz.

II. Temperatures Centigrade and Fahrenheit

Upon the centigrade scale, the freezing-point of water is 0° C. and the boiling-point 100° C. Upon the Fahrenheit scale, the same points are 32° F. and 212° F., respectively. The same interval is thus 100° on the one scale and 180° on the other. The degree Fahrenheit is therefore $100/180$ or $5/9$ of 1° Centigrade. Any temperatures can be converted by using the formulæ:

$$C.° = \tfrac{5}{9} \ (F.° - 32), \quad F.° = \tfrac{9}{5} \ (C.°) + 32.$$

III. Vapor Pressures of Water

Both the Fahrenheit (F.) or ordinary and the Centigrade (C.) temperatures are given.

Temperature.		Pressure, mm.	Temperature.		Pressure, mm.
F.	C.		F.	C.	
32°	0	4.6	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.2	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4	....	...	.....
69.8	21	18.5	212.0	100	760.0

IV. Prices of Important Chemicals

The prices quoted below are current prices in the New York market for January, 1923. Quotations in other cities or at other periods may, of course, vary considerably from the figures here given, particularly under abnormal conditions such as prevailed during the Great War. The student will find this table of service in considering the economic side of many industrial processes discussed in the text.

Acid, Acetic, glacial		
99.5% ....100 lb.		$12.00
Boric, crystals.....	lb.	0.11½
Hydrochloric,		
comm'l, 20°.......100 lb.		1.00
Hydrofluoric, 30%..	lb.	0.06
Hydriodic, sp. gr.		
1.150	lb.	2.25
Nitric, 42°	lb.	0.06
Phosphoric, 50%...	lb.	C.08
Sulphuric, 60°, tanks	ton	9.00
66°, tanks	ton	15.00
Oleum, 20%	ton	18.00
Alcohol, denatured....	gal.	0.40
Alum, potash	lb.	0.03½
Aluminium, 98-99%...	lb.	0.23
Ammonia, anhydrous,		
cylinders	lb.	0.30
Ammonium nitrate....	lb.	0.10
Ammonium sulphate..100 lb.		3.50
Aqua ammonia, 26°.	lb.	0.07

Antimony, ...100 lb.		$6.50
Arsenic, white	lb.	0.15
Bismuth	lb.	2.60
Blanc fixe, dry......	lb.	0.04
Bleaching powder,		
35% ....100 lb.		2.00
Borax, crystals	lb.	0.05½
Bromine, pure	lb.	0.28
Calcium carbide	lb.	0.04½
Calcium chloride, fused	ton	23.00
Calcium phosphate,		
mono	lb.	0.07
Carbon tetrachloride..	lb.	0.10
Chlorine, liquid, cylin-		
ders	lb.	0.06
Copper, electrolytic....	lb.	0.14
Graphite, high grade		
crude	ton	40.00
Iodine, resublimed.....	lb.	4.50
Lead ....,	lb.	0.07½
Lead, white, dry.....	lb.	0.08

Lithopone	lb.	$ 0.07
Magnesium, 99%	lb.	1.00
Mercury, flask	75 lb.	70.00
Nickel, electrolytic	lb.	0.36
Phosphorus, red	lb.	0.35
Phosphorus, yellow	lb.	0.30
Potassium bichromate	lb.	0.10
carbonate 80-85%	lb.	0.05½
chlorate, crystals	lb.	0.08
chloride, 80%	ton	35.00
hydroxide, 88-92%	lb.	0.07
nitrate	lb.	0.07
permanganate	lb.	0.17
Salt cake, bulk	ton	28.00
Silver	oz.	0.65

Soda ash, 58%	100 lb.	$ 1.80
caustic, 76%	100 lb.	3.50
Sodium acetate	lb.	0.07
bicarbonate	100 lb.	1.80
bisulphite	lb.	0.04
cyanide, 96-98%	lb.	0.23
nitrate, 95%	100 lb.	2.50
phosphate, di-	lb.	0.04
silicate, 40°	100 lb.	1.00
sulphide, 60%, fused	lb.	0.04
Steel bars	100 lb.	2.80
Sulphur, crude	ton	16.00
Tin	lb.	0.37
Zinc	lb.	0.08

INDEX

Acids are all listed under "acid" and salts under the positive radical.

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